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# RUBBER CHEMISTRY AND TECHNOLOGY

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## RUBBER CHEMISTRY AND TECHNOLOGY

RUBBER CHEMISTRY AND TECHNOLOGY is published quarterly under the supervision of the editors representing the Rubber Division of the American Chemical Society. The object of the publication is to render available in convenient form under one cover all important and permanently valuable papers on fundamental research, technical developments, and chemical engineering problems relating to rubber or its allied substances.

RUBBER CHEMISTRY AND TECHNOLOGY may be obtained in one of three ways:

- (1) Any member of the American Chemical Society may become a member of the Rubber Division upon payment of the dues (\$2.00) to the Division and thus receive RUBBER CHEMISTRY AND TECHNOLOGY.
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All applications for regular or for associate membership in the Rubber Division with its privilege of receiving this publication, all correspondence about subscriptions, back numbers, changes of address, and missing numbers and all other information or questions should be directed to the Secretary-Treasurer of the Rubber Division, Professor H. E. Simmons, Easton, Pennsylvania, or University of Akron, Akron, Ohio.

## To Our Readers

In spite of numerous important articles on rubber which have recently appeared in various domestic and foreign periodicals, this issue of **RUBBER CHEMISTRY AND TECHNOLOGY** contains only eight papers, all from American Chemical Society journals.

In fairness to our readers an explanation should be given to account for this sudden curtailment in the size of the **JOURNAL**, a change which it is hoped is merely temporary. As is known, it is possible to publish **RUBBER CHEMISTRY AND TECHNOLOGY** on any such scale as in the past only through the generosity of the Rubber Manufacturers' Association. This year there has been a delay in receiving our customary gift, and for lack of funds it has been necessary to publish a January issue in keeping with the state of the Rubber Division treasury. The character of this issue compared with recent issues will make one realize the dependence of the **JOURNAL** upon the kindness of the Rubber Manufacturers' Association, and the gratitude which is owed the latter organization for its generous support.

Whether or not the **JOURNAL** has fulfilled its mission of becoming a general compilation of important papers on the chemistry and technology of rubber, it has doubtless been of considerable value to the busy industrial chemist and technologist. It is hoped therefore that it may continue toward its goal of publishing under one cover, without the burden of foreign languages, all permanently valuable papers, and thus may contribute toward the greater proficiency of the technical staffs of the rubber industry.

THE EDITOR

# Rubber Division Activities

H. E. SIMMONS, Secretary-Treasurer of the Rubber Division of the American Chemical Society

## The Rubber Division of the American Chemical Society

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### Report of the Treasurer

Balance in the bank, September 1, 1931 (meeting at Buffalo).....	\$1270.92
Dues and Subscriptions from September 1 to January 1.	610.56
	\$1881.48

#### Expenditures:

Translations.....	\$ 155.50
Ben Franklin Printing Company.....	49.94
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Refund.....	45.00
Stenographic services.....	60.00
	1426.21

Balance in Bank, January 4, 1932.....	\$ 455.27
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H. E. SIMMONS, *Secretary-Treasurer*

## New Books and Other Publications

**Annual Report, 1930.** Published by the Rubber Research Institute of Malaya, Kuala Lumpur, F. M. S. 1931. 134 pp. \$1 (Malaya).

Considerable progress was made by the Rubber Research Institute of Malaya in the fifth year of its existence, despite the continued difficulty of a shortage of staff. In addition to the annual reports of the board and the director, there are presented the individual reports of the bacteriologist and the heads of the Experiment Station and of the Soils, Botanical, Pathological, Chemical, and Field Divisions. [From *The Rubber Age of New York*.]

**Organization of the World Rubber Markets.** By Franz Juda. 1931. 100 pp.

The author reviews the history of rubber marketing and gives able descriptions of the functions and status of the various types of firms participating in rubber distribution, including estate agencies, dealers, brokers, and manufacturers. With regard to the price of rubber, an intriguing chart is shown, from which the logical conclusion would be that at the present time a market price of 36d would result in an annual production of 1,000,000 tons of rubber, while a price of 3d would yield but 600,000 tons; against this, a 36d level would reduce consumption to 600,000 tons and a 3d level would raise consumption to 800,000 tons; the lines of production and consumption meet at the level of 5d. [From *The Rubber Age of New York*.]

**Sixth Annual Report—1931.** The Rubber Exchange of New York, Inc.

This pamphlet contains the brief annual report of the president of the Exchange and that of its treasurer. Trading on the Exchange for the year ended September 14, 1931, resulted in 38,529 contracts amounting to 220,995 tons. The present membership is 255, of which 203 are in the United States, 29 in England, 11 in France, 7 in Holland, 2 in Germany, and 1 each in Ceylon, China, and Australia. [From *India Rubber World*.]

**List of Members.** Published by the Institution of the Rubber Industry, Faraday House, 10 Charing Cross Road, London W. C. 2, England. 1931. 50 pp. For distribution to members.

That the Institution of the Rubber Industry has been able to increase its membership to 1374 as of last month compared with 1266 in September, 1930, is an indication of the regard in which its service is held by the British industry. The present roster shows the addition of Messrs. Boggs and Winkelmann to Fellowship in the Institution last year, an honor previously held only by Messrs. Bierer, Dinsmore, Geer, Somerville, Spence, and Wiegand in the United States. [From *The Rubber Age of New York*.]

**Reclaimed Rubber.** By A. T. McPherson. Published by the Bureau of Standards, United States Department of Commerce, Washington, D. C. 1931. 24 pp. \$0.10.

The need for some form of textbook covering the reclaimed rubber industry has long been felt. That need is not completely met by the present volume; but the author, who is chief of the Rubber Section of the Bureau of Standards, has at least prepared a careful review of the principles of reclaiming operations and of the properties and uses of reclaim. Intended primarily to be of general interest and to answer the numerous questions asked of the Bureau in regard to reclaim, this handbook nevertheless contains much technical detail with respect to processes for reclaiming and the characteristics of the product, such as tensile strength, elongation, abrasion resistance, and aging. The author rightly discourages individuals who wish to undertake the reclaiming of rubber on a small scale, pointing out the neces-

sity for special equipment and skilled technical control. He concludes with a bibliography of technical magazine articles. [From *The Rubber Age of New York*.]

**Rubber and Railways.** By Colin Macbeth. Published by the Rubber Growers' Association, Inc., 2 Idol Lane, Eastcheap, London, E. C. 3, England. 1931. 68 pp. For free distribution.

Railroad engineers, in constantly striving after greater traveling comfort and more efficient operation, have already found wide use for rubber products, and Mr. Macbeth is hopeful that the amount of rubber employed may be extended. The commercial possibilities in this field may be estimated from the fact that some British passenger coaches use over 600 pounds of manufactured rubber while a locomotive and tender unit sometimes makes use of nearly 150 pounds. Mr. Macbeth devotes separate chapters to rubber on British, American, and French railroads and finds that his native country has gone far ahead of the other two nations in the successful adoption of rubber for railroading. The author has, however, omitted mention of the use of rubber absorption pads by the Canadian Pacific, the development of the Goodyear rubber-cushioned wheel tested this year on the Akron, Canton & Youngstown Railway, and the use of rubber belts between car wheels and lighting system dynamos. The Avery elastic rubber spring is a development of recent months that also holds much promise for the future. [From *The Rubber Age of New York*.]

**A. S. T. M. Tentative Standards 1931.** American Society for Testing Materials, 1315 Spruce St., Philadelphia, Pa. Paper or cloth, 1008 pages, 6 by 9 inches. Indexed. Illustrated.

This volume contains 180 tentative standards, 30 of which relate to rubber products, insulating materials, and textiles. There is a comprehensive subject index and a table of contents which lists, under the various materials covered, the respective standards. In addition a complete list of all the standards and tentative standards of the society in effect September 1 is included. [From *India Rubber World*.]

**1931 Supplement to Book of A. S. T. M. Standards.** American Society for Testing Materials, 1315 Spruce St., Philadelphia, Pa.

This 144-page pamphlet, the first supplement to the 1930 Book of A. S. T. M. Standards, contains 32 standards adopted or revised by letter ballot of the Society on September 1, 1931. It also contains a list of Standards and Tentative Standards as of September, 1931; of these, 443 are of the former class and 180 of the latter; total, 623. [From *India Rubber World*.]

**Symposium on Abrasion Testing of Rubber.** American Society for Testing Materials, Philadelphia, Pa.

This authorized reprint from the proceedings of this society includes the papers and the discussions on abrasion testing of rubber presented at the Thirty-fourth Annual Meeting of the A. S. T. M. held in Chicago, June 22-26, 1931. Five papers are included in which are discussed the results obtained by several types of abrasion machines. The symposium has focused attention on the requirements for an ideal abrasion test and, it is expected, will stimulate study that will result in accomplishing great improvements over present methods for abrasion testing of rubber. [From *India Rubber World*.]

**Methods of Test Relating to Electrical Insulating Materials.** Published by the American Society for Testing Materials, 1315 Spruce Street, Philadelphia, Pa. 1931. 216 pp. \$1.25.

In addition to the current report of Committee D-9 of the A. S. T. M., this annual

volume contains the methods of testing insulating materials that have been developed by the society. Three standard methods and ten tentative methods of test are given. The volume also includes ten specifications covering certain rubber and textile products which should be of interest. The specifications included cover friction tape, rubber insulating tape, rubber gloves, rubber matting, and other materials. [From *The Rubber Age* of New York.]

**Colloid Chemistry.** Vol. III. Edited by Jerome Alexander. Published by the Chemical Catalog Company, 419 Fourth Avenue, New York City. 1931. 655 pp. \$10.50.

The first two volumes of this series dealt with theory and methods and with biology and medicine, respectively, and it is the intention of the last two to describe technological applications. The present volume contains 42 papers on general principles, mechanical or more specialized matters, and on applications relating to geology, mineralogy, metals, petroleum, and agriculture. Of particular interest to rubber technologists is the paper by P. P. von Weimarn on the "Rubber-Like and Liquid-Crystalline States of Matter, in Connection with the Classification of Crystals and Molecules according to Their Vectoral Fields." Professor George L. Clark also treats briefly on rubber in his paper on x-ray researches on colloids. The fourth volume of this series, which is soon to be published, will devote more space to work with rubber and other plastics. [From *The Rubber Age* of New York.]

**Chemistry of Engineering Materials.** Robert B. Leighou. McGraw-Hill Book Co., Inc., New York and London, 1931. 3rd Ed. Cloth, 684 pages, 5 $\frac{1}{4}$  by 8 inches. Illustrated. Indexed.

This work, one of the popular International Chemical Series texts, has been newly revised to bring the subject-matter into conformity with the advances made in the past 6 years. The author presents to his readers a brief yet comprehensive and up-to-date account of the nature, origin, and industrial applications of the raw materials of modern industry.

In the chapter on rubber, 19 pages are given to a condensed and accurate view of the sources and the preparation of crude rubber, methods of its vulcanization, the functions of accelerators, and other materials used in compounding soft rubber and ebonite. Reclaims, synthetic rubber, and factice are also briefly considered. The work is as closely up-to-date as can well be expected considering the rapid pace of current industrial development. [From *India Rubber World*.]

**Chemical Engineering Catalog.** Sixteenth Edition. Published by the Chemical Catalog Company, 419 Fourth Avenue, New York City. 1931. 1017 pp. \$10.

There has been considerable development in the amount of detailed information presented in the pages of this standard reference work, although the actual number of manufacturers represented shows a slight decrease. The current volume contains, as usual, collected, condensed, and standardized catalog data of equipment, machinery, laboratory supplies, heavy and fine chemicals and raw materials, with classified indices, carefully cross-referenced, and a technical and scientific book section, cataloging and briefly describing an extensive list of books in English on chemical and related subjects. It is as much as ever essential for chemical engineers, works managers, purchasing agents, and others who buy and specify equipment and materials in chemical process industries. [From *The Rubber Age* of New York.]

# A Survey of Recent Literature on the Chemistry of Rubber

## Abstracts of Articles Pertaining to the Chemistry of Rubber Which Have Appeared in Foreign and American Journals

The following abstracts are reprinted from the October 10 and 20 and November 10 and 20, 1931, issues of *Chemical Abstracts* and with earlier and succeeding issues, they form a complete record of all chemical work published in the various academic, engineering, industrial, and trade journals throughout the world.

**The chemist in the rubber plant.** BERT S. TAYLOR. *J. Chem. Education* 8, 1829-38(1931). E. H.

**Modern progress in rubber compounding.** CHARLES R. BOGGS. Signal Section Am. Railway Assoc., Pamphlet May 13, 1931, 26 pages.—A review and discussion, with particular reference to recent improvements in the phys., elec. and aging properties of rubber insulation, and with the inclusion of new data on the aging of new types of rubber mixts. By curing with tetramethylthiuram disulfide with or without Se or Te, and in the absence of S, vulcanizates are obtained which have an extraordinary span of life in O under pressure at 70°, *i. e.*, age better than any mixts. vulcanized with S. Thus the base mixt.: rubber 100, ZnO 100, whiting 100, "Agerite powder" 2, paraffin 5, stearic acid 1, cured with (1) tetramethylthiuram disulfide 3; (2) tetramethylthiuram disulfide 1.5, Te 0.5 and (3) tetramethylthiuram disulfide 1.5, Se 0.5, deteriorated little on treatment with O under 300 lb. per sq. in. pressure at 70° for 960 hrs. A corresponding base mixt. cured with S 3 and mercaptobenzothiazole 0.6 was in relatively poor condition. In elec. properties vulcanizates can now be made with dielec. strengths of 200-1200 v. per mil, power factors of 0.5-25%, resistivities of  $1 \times 10^6$  to  $5000 \times 10^6$  megohms per cm. cube, and dielec. consts. as low as that of gutta-percha (2.7-3.0). Data show that these vulcanizates have excellent elec. properties after long immersion in water. In conclusion, there is a discussion of performance specifications instead of the type prevailing at the present day (cf. Bierer and Davis, *C. A.* 22, 883).

C. C. DAVIS

**Concentrated latex.** RUDOLF DITMAR. *Caoutchouc & gutta-percha* 28, 15607-8 (1931); cf. *C. A.* 25, 4737.—Forty-nine German, U. S. and British patents are listed, with a brief discussion of some of them. C. C. DAVIS

**Microturbidimeter for determination of rubber content of latex.** S. D. GEHMAN AND J. S. WARD. *Ind. Eng. Chem., Anal. Ed.* 3, 300-4(1931).—The fact that the hydrodynamic method and also trial coagulation methods for detg. the dry rubber content of latex have certain shortcomings induced the authors to develop a turbidimetric method. This method depends upon the fact that the turbidity of latex depends upon the no. and size of the suspended rubber particles, and therefore the turbidity can under suitable conditions be utilized as a measure of the rubber content of the latex. A microturbidimeter, which is a modification of that of Conklin (cf. *C. A.* 19, 2284), was developed for this purpose. The method is more rapid than the 2 trial coagulation methods, and though its precision is less than the lengthy trial coagulation method (coagulation, creping and drying), the precision is probably greater than the shorter trial method (coagulation and creping); the precision is approx. 1% rubber in 35% latex. The use of color filters, which transmit the shorter wave lengths, minimizes the effects of a difference in the effective mean particle size of different kinds of latex. The turbidity of latex obeys the turbidity-diln. law when the rubber content is below 15%. C. C. DAVIS

**Hard and soft rubber for pickling tanks.** H. E. FRITZ. *Chem. Met. Eng.* 38, 396-7(1931).—An illustrated description of the most recent developments, with special reference to linings for use with  $H_2SO_4$ . In nearly all pickling operations, small quantities of oil are encountered at the surface, and since hard rubber is the only form with good resistance to oil, a combination of hard and soft vulcanized rubber was developed.

In this new construction the hard and soft rubber plies are overlapped so that virtual expansion joints are formed. The application of this construction to wood and steel tanks, by the Vulcalock process, is described, with a comparison of the relative merits of wood and steel constructions.

C. C. DAVIS

**New autographic machine for testing tensile properties of rubber.** GEORGE J. ALBERTONI. *Ind. Eng. Chem., Anal. Ed.* 3, 236-9 (1931).—The machine which is described and illustrated in detail records the stress-strain curve of a highly deformable material, and is so equipped that variations in the cross-sectional areas of test specimens are mechanically corrected. In this way the personal equation in testing is reduced to a min., and the stress-strain curves obtained are directly comparable without any calcs.

C. C. DAVIS

**Identifying rubber quantitatively in compositions of rubber and asphalt. The new "ebonite method."** F. C. VAN HEURN AND M. A. BEGHEYN. *India Rubber J.* 81, 847-51 (1931).—The method described is applicable to uncured mixts. and to mixts. at any state of cure. It depends upon the fact that whereas at 150° S reacts with rubber to form hard rubber, it does not react with asphalt below 175°. Therefore, at 140-60° rubber with sufficient S can be transformed into a product which because of its insol. in all org. solvents allows extn. of the asphalt. Preliminary expts. on the influence of the proportion of S, the temp., the time of reaction and the solvent, which are described in detail with quant. data, led to the following recommended procedure: Ext. the sample (a wt. corresponding to 50-100 mg. of rubber) with xylene for 8 hrs., evap. the ext., heat the residue with S (twice the wt. of the original sample) for 4-5 hrs. at 160° (if H<sub>2</sub>S is evolved, a lower temp. and a longer time must be used) with hourly stirring, cool, ext. the reaction mixt. with xylene and dry and weigh the residue at 150°. The S content of this residue is then detd. as follows: Add to the residue (100 mg.) an oxidizing soln. (10 cc. of a mixt. of 1000 cc. of HNO<sub>3</sub> (d. 1.4) and 200 g. of ZnO, satd. with Br), let stand several hrs., add fuming HNO<sub>3</sub> (15 cc.), when soln. is complete add Br water (5 cc.), conc. to a syrup (if org. particles remain, add a few cc. of fuming HNO<sub>3</sub> and evap. again), cool, add KClO<sub>3</sub> (a few crystals), heat until evapd. and no more nitrous vapors are evolved, heat the residue gently with 6-7 cc. HCl (d. 1.19), dil. with water, filter and det. the S as BaSO<sub>4</sub>. If the content of impure hard rubber is *a* % of the sample, and the S content is *b* %, then the rubber content of the material analyzed is:  $0.68 \times (b/32) \times a = 0.02125 ab \%$ . C. C. DAVIS

**The varnishing of rubber footwear.** H. KOCH. *Gummi-Ztg.* 45, 1683-6 (1931).—A review and discussion. "Also in *Rubber Age* (London) 12, 251-3 (1931)."

C. C. DAVIS

**The examination of rubber substitutes.** GRANDEL & CO. *Rubber Age* (London) 12, 210-4 (1931).—See *C. A.* 25, 4441.

C. C. DAVIS

**Increase in the resistance to abrasion of rubber products vulcanized by stannous selenide and cadmium selenide.** R. DITMAR AND K. H. PREUSSE. *Cauchooc & gutta-percha* 28, 15639-40 (1931); cf. *C. A.* 25, 2593.—SnSe and CdSe were tested in rubber-S mixts. and in accelerated mixts. In rubber-S mixts. neither SnSe nor CdSe had any plasticizing, accelerating or reenforcing action. In the same accelerated mixts. as those used in the earlier work on PbSe, their action was similar to that of PbSe, for with the majority of accelerators each had a notable reenforcing action and increased the resistance to abrasion. In mixts. vulcanized with S<sub>2</sub>Cl<sub>2</sub>, neither SnSe nor CdSe had any particular effect. In general, SnSe and CdSe are superior to the Se.

C. C. DAVIS

**Latex.** E. BĚLAVSKÝ AND B. MAKARIUS. *Chem. Obzor* 6, 137-8 (1931).—A new method is proposed for the detn. of rubber in latex or in similar preparations. Proteins (casein) are removed by the enzymic method prior to coagulation by 50% AcOH at 36-40°, in which tryptase and ereptase are the substantial proteolytic enzymes.

J. KUČERA

**The gelatination of latex and "Revertex" by means of extremely concentrated aqueous solutions of substances appearing as dispersators for proteins.** P. P. VON VEIMARN. *Proc. World Eng. Cong., Tokyo 1929* 31, 473-80 (1931).—The pptn. of *Hevea* latex or properly diluted Revertex in extremely concd. solns. of LiI, LiCNS, Ca(CNS)<sub>2</sub>, NaI, Ca(NO<sub>3</sub>)<sub>2</sub>, CaCl<sub>2</sub>, etc., of polyphenols, e. g., pyrogallol and resorcinol, thiourea and guanidine thiocyanate was studied at temps. up to 170°. LiI and LiCNS were the most powerful dispersators. A complete expt. with LiI is described. Gelatination is almost immediate. Micro and ultra-microscopical observations on the process of gelatination are given.

ALDEN H. EMERY

**The hydrogen-ion concentration of *Hevea* latex.** N. H. VAN HARPEN. *Arch. Rubbertuin* 15, 1-67 (1931) (in English 68-102).—Methods (macro and micro) for

detn. of H-ion concn. are discussed in great detail. The effect of autoacidification, evapn., and the addn. of coagulating agents on the acidity and the application of the method to the study of centrifuging, to latex contg. HCHO (I), coagulation with lactic acid (II) and Na biformate (III) and the alkalimetric titration of latex are described. Autoacidification occurs to a degree depending upon the compn. of the serum of the latex and upon the disinfectant action of the coagulant. Mineral acids hinder autoacidification, and much more regular values are obtained at low degrees of acidity than with AcOH (IV) or  $\text{HCO}_3\text{H}$  (V), which possibly promote autoacidification but which in higher concns. hinder it. Evapn. leads to an increase in the degree of acidity, provided the coagulant does not evap. to the same extent. Addn. of a coagulant also increases the degree of acidity. If to a given vol. of latex a certain quantity of coagulant is added, the soln. has a lower degree of acidity than the same vol. of water contg. the quantity of coagulant. The expts. show that the surface of the dispersed rubber particles plays the most important part in this adsorption. If  $s$  is the quantity of H ions adsorbed,  $q$  the increase in the  $\rho_{\text{H}}$  value by evapn.,  $p$  and  $r$  the diminutions in  $\rho_{\text{H}}$  by autoacidification and addn. of the coagulant, resp., and if all are expressed as neg. logarithms of the H-ion concn., then the increase in the degree of acidity at any diln. is:  $\Delta\rho_{\text{H}} = -p - q - r + s$ . With no coagulant, autoacidification was considerable at first, but became negligible at higher acidity. A coagulum was obtained with a dry rubber content above 15.2% when the  $\rho_{\text{H}}$  value diminished to approx. 6.5, though a clear serum was not obtained. The greatest decrease in  $\rho_{\text{H}}$  was with undil. latex, where the increase in acidity was  $5.78 \times 10^{-7}$ , and from, this calcns. show that  $\Delta\rho_{\text{H}}$  is influenced only by  $r$  and  $s$  in the equation above. The value of  $r$  is detd. by a blank expt., and therefore the variation of  $\Delta\rho_{\text{H}}$  depends upon  $s$ , since  $r$  is const. The calcns. also show that the deviation of the adsorption curves when  $\rho_{\text{H}}$  is above 5 (as shown by IV and V latex mixts.) can be due only to autoacidification. When these org. acids were increased, the degree of acidity of the dispersion diminished, while the addn. of a small quantity compared with the same quantity of mineral acids promoted autoacidification, with increase in the degree of acidity. Fresh field latex coagulated in approx. 10 hrs., with formation of a white serum which became cloudy after 48 hrs. Cream could not be coagulated, even after 48 hrs. with accompanying autoacidification, for the dispersion remained in a state of loose particles close together and coalescence did not occur. Underlatex coagulated spontaneously in 0.25 hr., with formation of a cloudy serum. The cream had a lower H-ion concn. than the field latex ( $\rho_{\text{H}}$  7.25 and 6.90, resp.), whereas the underlatex had a much higher degree of acidity ( $\rho_{\text{H}}$  8.56 and 6.90, resp.). In the adsorption expts. with coagulants, the underlatex adsorbed H ions more strongly than field latex, and the latter more strongly than cream with the same dry rubber content. Cream and field latex were more nearly similar. With cream, the boundary of the 2nd liquid stage and the 2nd coagulation stage lay at a higher  $\rho_{\text{H}}$  value than with field latex of corresponding concn., and the boundary of the 1st liquid and 1st coagulation stage also lay at a higher  $\rho_{\text{H}}$  value. The serum of cream also first became clear at a lower degree of acidity than did that of field latex. Cream flocculated more easily than field latex, while underlatex did not flocculate. Upon the addn. of coagulants, latex contg. I formed flocculates, and there was some factor which hindered gel formation and made the phenomenon differ from that with fresh latex. Latex contg. I adsorbed H ions less strongly, which indicates that the adsorptive surface of the latex contg. I is reduced. In expts. where increasing proportions of I were added to latex (both dild. and undild.) contg. NaOH, the addn. of I stabilized the dispersion for many hrs. or even days longer than without its addn. Addn. of acid first caused flocculation, but all flocculates coalesced after standing. When the max. time of preservation was exceeded, autoaggregation speedily occurred, and besides loose flakes, streaks and lumps of coagulum sepd. Twenty cc. of com. HCHO per 1. of latex prevented flocculation for over 1 month, and upon the addn. of a coagulant no coagulum was formed. The stiff, compressed flakes agglomerated only upon addn. of concd. HCl to a  $\rho_{\text{H}}$  value of 4.0. With latexes contg. 0.5, 1 or 2 cc. of com. I per 1., the boundaries of the 1st liquid and 1st coagulation stage were displaced to a lower degree of acidity, and in this respect latex contg. I resembles the centrifuged cream. In detg. the rubber content of latex contg. I, difficulty was encountered by the flocculates which could not be coalesced. Inoculation with fresh latex or  $\text{NH}_4\text{OH}$  and subsequent addn. of a coagulant gave a coagulum, the rubber in which could be easily detd. The behavior of a new coagulant can be judged by detg. its dissociation in water and the adsorption of H ions with latexes of various concns. II behaves like V when the comparison is made on a mol.-wt. basis. The addn. of III forms a buffer soln. with V, with a lower degree of acidity than the

corresponding quantity of V without a salt constituent. The addn. of water to the buffer soln. has, however, less effect than upon the unbuffered V soln. If III is added to latex, the H ions are adsorbed, and coagulation is either complete or incomplete, depending upon the remaining degree of acidity of the serum. Adsorption expts. showed that the coagulation boundary of the III buffer soln. in latex contg. 15-20% rubber is reached with 1.14-2.28 g. of III per l. The cost of III therefore makes its use very uneconomical. The only precise method for detg. the neutralization point and the potential degree of acidity of latex is by electrometric titration. The following was developed as the most practical method. Dil. the latex to 10 times its vol., remove 20 cc., to the latter add a few drops of phenolphthalein (VI), titrate with 0.5 N  $H_2SO_4$  until no longer red (with latex quinhydrone gives unreliable results when  $pH$  is above 8.0), add excess quinhydrone, make an initial detn., then make detns. rapidly with continual addn. of acid and stirring until with the app. recommended the disconnecting point at the end of the sliding scale is reached, change the H half-cell with the calomel electrode, take the const. reading on the scale for 1 min. with const. agitation, and titrate with addn. of small quantities of 0.5 N  $H_2SO_4$  until the neutralization point is exceeded. This excess is shown at once by a great change on the scale when acid is added. The dispersion can be kept in const. motion throughout by a rotating elec. stirrer. Old latexes preserved with  $NH_3$  coagulate very rapidly when the acidity goes above the neutral point. Ammoniated latex of different concns. and with different proportions of  $NH_3$  was studied. Differences between ammoniated latex and dil. aq.  $NH_4OH$  were very small, and big deviations were the result of auto-acidification. With VI and Me red, the titrations showed particularly large variations with ammoniated latex, but gave values either below or above the quantity of 0.5 N  $H_2SO_4$  for neutralization ( $pH = 6.91$ ), depending upon the  $p_B$  value at the transition point of the indicator. By electrometric titration in latex preserved with alkalies a precise detn. of the preservative is possible, the detn. of the neutral point can be made for any fixed temp., and the quantity of acid to reach a certain point on the scale can be read immediately. A further application is in the calcn. of the most economical quantity of coagulant for the prepn. of sheet or crepe from latex preserved with alkalies. Because of the formation of buffer solns. from preservatives, it is impossible to det. directly with any certainty the quantity of coagulant for a given vol. of latex. In place of the  $pH$  value of 6.91 of the neutral point, it is possible to fix the desired degree of acidity for satisfactory coagulation. This point can be fixed on the scale by a short calcn.

C. C. DAVIS

**Crystallized rubber.** R. PUMMERER AND G. VON SUSICH. *Kautschuk* 7, 117-9 (1931).—A review and discussion of recent work on the crystn. of rubber by methods other than by stretching, with certain hitherto unpublished observations. Crystn. by methods other than stretching may be divided into 3 general processes: (1) spontaneous crystn. under conditions little or no different from normal, e. g., by "freezing" on storage, (2) crystn. from soln. after purification and (3) crystn. of a soln. of purified rubber by cooling to low temps. The conditions which govern "freezing" are little known. Cooling alone does not bring about freezing in a short time, for smoked sheet and evapd. latex were kept for 8 days at approx.  $-190^\circ$  while unstretched, and then showed only amorphous x-ray diagrams. Rubber previously mildly racked and cooled to  $-190^\circ$  also showed no cryst. interferences, but only evidence of ice crystals. The expts. of Ott (cf. *C. A.* 25, 434) could not be confirmed. The x-ray irradiation of 20 different kinds of crepe (elastic, with no symptoms of freezing) showed crystals in nearly all cases in the unstretched condition. Spontaneous crystn. of crepe therefore takes place much more readily than crystn. in smoked sheet; this is attributed to the higher degree of purity of crepe. There is considerable evidence that crystd. rubber is closely related to  $\alpha$ -gutta-percha or perhaps identical with it. For example, on x-ray irradiation an old sample of crystd. rubber gave a Debye-Scherrer diagram identical with that of  $\alpha$ -gutta-percha. When the old crystd. rubber was warmed to  $70^\circ$  during the irradiation the diagram became amorphous, while upon cooling again the Debye-Scherrer diagram of  $\beta$ -gutta-percha appeared. It is considered that the reputed prepns. of cryst. rubber by the U. S. Bur. of Standards (cf. Wolf, *C. A.* 25, 232) is open to question, particularly since the optical behavior, x-ray diagrams, m. p., etc., are not known. In expts. by P. in which a 1%  $Et_2O$  soln. of rubber-sol at  $-70^\circ$  was irradiated with x-rays, the liquid solidified completely, but there were no cryst. interferences. Therefore in spite of these ppts. being fibrous, they are not rubber crystals, but only solidified rubber- $Et_2O$  gels (as in the cooling of concd. gelatin solns.). As a general conclusion it is considered that crystd. rubber has not yet been ptd. from soln. by

purification and cooling to low temps., and that so far it has been obtained only from stretched and "frozen" crepe rubbers.

C. C. DAVIS

**The law of degradation of rubber solutions as a function of the time at different temperatures.** P. BARY AND E. FLEURENT. *Compt. rend.* 192, 946-8 (1931).—It has already been shown (cf. *C. A.* 21, 2398) that when rubber is heated at slightly elevated temps. the mol. transformation does not involve any change in chem. compn. and is reversible. At const. temp., the viscosity (measured by the time of flow through a capillary) of rubber solns. diminishes with time, more or less rapidly according to the temp., and reaches very low values which approach those of the pure solvents. Unlike that in the earlier expts., this change is irreversible. Though the viscosity of the solns. does not have an exact phys. meaning, since it depends upon the rigidity of the soln., its values are related directly to the degree of dispersion of the rubber. Whatever the structure of the disperse phase (polymeric, micellar, etc.), the reduction in the apparent viscosity corresponds to a degradation  $D$  of this structure. Then  $D = 1/(\eta - 1)$ , where  $\eta$  is the viscosity of the soln. in relation to that of the solvent as 1. Expts. at 20°, 40° and 55° for 5000-6000 hrs. show that the degradation of rubber in soln. increases rapidly with increase in temp., and that to ascertain the general law, the temp. must be maintained as nearly const. as possible. Accordingly, data were obtained on  $C_6H_6$ , PhMe and xylene solns. of pale crepe (extd. with  $Me_2CO$ ), which were tested at the b. ps. of  $C_6H_6$  and xylene, and on a boiling water bath with PhMe. The data show that the hyperbolic equation:  $(\eta - 1)(t + \theta) = A$ , represents the viscosity  $\eta$  as a function of the time  $t$  (in hrs.), where the const.  $\theta$  may be pos. or neg. (depending upon the point chosen to begin the measurements) and  $A$  is a const. which is characteristic of the solvent and of the temp. Replacement of  $(t + \theta)$  by  $T$  and of  $\eta - 1$  by  $1/D$  gives:  $T = AD$ . The following data give the solvent, the temp.,  $A$  and  $T$ , where  $T$  is the no. of hrs. for the rubber soln. (2 g. in 100 cc.) to reach a viscosity at 15° 10% greater than that of the solvent:  $C_6H_6$ , 80°, 3540, 35,400; PhMe, 93.5°, 58.78, 587.8; xylene, 138-40°, 18.15, 181.5. With xylene, the temp. was so high that the degradation was accompanied by a chem. change, apparent when the soln. turned dark red and acquired a distinctly new odor.

C. C. DAVIS

**The problem of the effect of selenium in rubber mixtures.** H. RIMPEL. *Kautschuk* 7, 94-7 (1931).—Systematic expts. were carried out to det. whether the claim of Boggs and Follansbee (cf. *C. A.* 21, 1566) that Se increases the resistance of a vulcanize to abrasion could be substantiated. R. used the more reliable Williams method (*C. A.* 21, 2573; 23, 3132) of comparing resistances to abrasion on the basis of work expended in preference to the method of B. and F. based on vol. losses, and found that Se does not increase the resistance to abrasion in the way claimed by B. and F. To the base mixt.: smoked sheet 100,  $ZnO$  50, were added (1) S 5,  $MgO$  1; (2) S 3, Se 3,  $MgO$  1; (3) S 5, diphenylguanidine 0.5, and (4) S 3, Se 3, diphenylguanidine 0.5; the vulcanizates in different states of cure, including the optima, were tested comparatively for resistance to abrasion. At the optimum cures, the resistances of (2), (3) and (4) were virtually the same; that of (1) poorer. Without org. accelerator, Se improved the resistance to the same extent as did the accelerator at a shorter cure, but no more so, and with org. accelerator Se was of no benefit. The *P* 53, *P* 54 and *P* 77 vulcanizates of B. and F. (*loc. cit.*) were also tested. Here at the optimum cures, Se increased decidedly the stiffness (modulus) of the stress-strain curve and the hardness (7-10% increase), and lowered the tensile strength (approx. 12%). In one case Se improved the resistance to abrasion a little, in the other diminished it, and in general it was considered of no material benefit. The vulcanizates contg. Se also had disproportionately high d., and this effect was proved to be present before vulcanization (cf. Kirchhof, *C. A.* 25, 1410). Similar expts. with the mixt.: smoked sheet 100, S 5,  $PbO$  30, gas black 40, with and without Se 3, showed that in this type of mixt., also, Se does not improve the resistance to abrasion, tends to make the stress-strain curve less stiff rather than stiffer as before, and reduces the tensile strength considerably. Here, too, the Se mixt. had a disproportionately high d. Practically the same results were obtained with lamp black in place of gas black. Accordingly the failure to stiffen is attributable to the joint effect of Se and  $PbO$ , just as the stiffening action with diphenylguanidine may be attributed to its joint effect with Se. This stiffening action does not vary with the accelerating activity, for with very high proportions of diphenylguanidine and with a more powerful accelerator, the stiffening action was not proportionately greater. To det. whether without S, the effect of Se would be greater, the base mixt.: pale crepe 24,  $PbO$  6,  $ZnO$  12, whiting 30, was cured with (1) Se 3.4,  $ONC_6H_4NMe_2$  1, and (2) S 1.2. The tensile properties, hardness, d. and resistance to abrasion of each vulcanizate were then detd. Here at each cure the vulcanizate cured with S had a higher tensile

strength, a higher ultimate elongation and a much greater resistance to abrasion, and was slightly softer than the vulcanizate cured with Se. C. C. DAVIS

**Titanium oxide in rubber mixtures.** R. DITMAR. *Caoutchouc & guita-percha* 28, 15640-3(1931).—Rubber contg.  $TiO_2$  when cured either by  $S_2Cl_2$  vapor, or by dipping in a  $CS_2$  soln. of  $S_2Cl_2$ , must be cured slightly longer than without  $TiO_2$  under the same conditions, and the products contg.  $TiO_2$  are more supple, and of an excellent white color. In curing by the hot method with org. accelerators,  $TiO_2$  is a satisfactory substitute for  $ZnO$  as an activator, but in spite of this it retards the rate of vulcanization slightly because it is a strong plasticizing agent. Because of this plasticizing action, the greatest activation can be obtained by using a relatively small proportion in conjunction with  $ZnO$ . Advantage may, however, be taken of this plasticizing effect of  $TiO_2$ , and the tendency of uncured rubber mixts. to "scorch" be prevented by a sufficient quantity of  $TiO_2$ . C. C. DAVIS

**Accelerators of vulcanization.** F. JACOBS. *Caoutchouc & guita-percha* 28, 15602-7 (1931); cf. *C. A.* 25, 4442.—The general actions of tetraethylthiuram disulfide, aldehyde-amines and hexamethylenetetramine as accelerators are discussed, with representative quant. data. *Ibid* 15638-9.—The properties and general behavior as an accelerator of aldehyde-ammonia are described, with quant. data. C. C. DAVIS

**Effect of "Catalpo" on the physical properties of vulcanized rubber.** YOSHIO KATO AND MUNEHARU EGAWA. *Repts. Imp. Ind. Research Inst. Osaka, Japan* 12, No. 3, 38 pp.(1931).—The effect of "Catalpo" on the phys. properties of vulcanized rubber depends upon the type of Catalpo used. The best results are obtained if the Catalpo has the following properties:  $Al_2O_3$  above 31%;  $SiO_2$  below 45%; water (water of crystn.) 14-18%, and uniformity in the size of the particles. F. I. N.

**Manufacture of concentrated latex by the Revertex process.** GEORGES GENIN. *Rev. gén. mat. plastiques* 7, 329-33(1931).—The advantages of the use of concd. latex over coagulated rubber are discussed. It is claimed that the Revertex process has successfully solved the problem of drying latex without destroying the colloidal state. It consists essentially in low-temp. evapn. by the Krause spray process in presence of a protective substance (not disclosed) to prevent irreversible flocculation. A cheap substance has been discovered for this purpose which can be easily prepd. at the plantations, and the evaporator has been modified so as to make it practical for use at the plantations. A. PAPINEAU-COUTURE

**Microporous rubber, its preparation, properties and use.** H. BECKMANN. *Kautschuk* 7, 149-55(1931).—A review and discussion of the work of B., which is covered by numerous patents. C. C. DAVIS

**Behavior of carbon black as a rubber filler in relation to its adsorption of methyl violet.** E. V. REUTER. *Kautschuk* 7, 132-4(1931).—The expts. were suggested by those of Fromandi (*C. A.* 24, 3395). The adsorptive power of various types of C blacks for aq. methyl violet varied directly with the reenforcing action of the blacks in vulcanized rubber. To det. the relation between adsorptive power and structure, the data of Péterfi (*Kautschuk* 3, 196(1927)) were utilized in calcns. which show that the total surface area per unit wt. of black (a cylindrical particle is assumed) varies directly with the absorptive power for methyl violet. Phys. tests of vulcanizates contg. the blacks are shown graphically. C. C. DAVIS

**Colors used in the rubber industry.** G. F. THOMPSON AND E. V. BRATBY. *J. Oil and Colour Chem. Assoc.* 14, 218-41(1931).—The transition from the use of pigments in rubber for decorative purposes to their more important use as compounding ingredients is discussed. The demands upon pigments are severe because of the dark color of the rubber itself, the effects of the various curing processes upon the pigments and the effects of certain elements, e. g., Cu, Mn, Cr upon the aging of the rubber. Pigments should be uniform in size and not over  $10\mu$  in diam. They should not be flat or elongated as such particles tend to agglomerate. The suitabilities of a no. of pigments are individually discussed. G. G. SWARD

**Rubberizing of textiles with latex.** RUDOLF DITMAR. *Kolloid-Z.* 56, 124-5 (1931).—Patent review.

**The behavior of rubber with textile fabrics and fibers.** WERNER ESCH. *Kautschuk* 7, 155-6(1931).—A discussion of certain features of the impregnation of textiles with latex and with rubber solns. C. C. DAVIS

**The appearance of atmospheric cracks in stretched rubber.** A. VAN ROSSEM AND H. W. TALEN. *Kautschuk* 7, 79-86, 115-7(1931).—The expts. show that "sun-cracking" is not caused by sunlight but by atm.  $O_3$ , and takes place only when the rubber is under tension. Vulcanizates of different compns. under various degrees of elongation exposed to air and light showed max. cracking at 10-20% elongation, and this cracking

occurred at the same rate and was of the same nature when the expts. were repeated in darkness. The term sun-cracking should therefore be abolished in favor of *atm. cracking*. There was no cracking when the vulcanizates were not stretched. Exposure to air contg. O<sub>2</sub> also caused cracking (again only when the samples were stretched), so that ultra-violet light is not necessary (cf. Krahl, *C. A.* 21, 2816), and the explanation of Kearsley (*C. A.* 24, 4957) is untenable. There was no cracking on exposure in air contg. N oxides, SO<sub>2</sub> and Cl. The formation of cracks by O<sub>2</sub> suggests a *sensitive, sp. reaction for O<sub>2</sub>*. Cracking does not depend upon the type of rubber, its degree of mastication, the coeff. of vulcanization, the particular filler or pigment or the particular accelerator, whereas the character of the stress-strain curves (modulus) has a determinant influence on the size and extent of cracking. No softener or org. diluent of numerous ones tested was of benefit when the O<sub>2</sub> concn. was above 0.003%, but below this concn. those which formed a surface bloom, *e. g.*, paraffin, had a protective action. Fe applied in various forms to the surface (ink, rust, etc.) had no influence on cracking. A repetition of Williams' expts. (cf. *C. A.* 20, 2093) on the prevention of cracking by CuCl<sub>2</sub> on the surface failed to confirm his results. C. C. DAVIS

**Reaction of sulfur dioxide and hydrogen sulfide in hydrocarbons.** PAUL BARY. *Rev. gén. caoutchouc* 8, No. 71, 25-6 (1931).—The 1st stage in the reaction of rubber and S is soln. of the S in the rubber, and since colloidal S is an insol. form at room temp., it is unlikely in the Peachey process of curing rubber with SO<sub>2</sub> and H<sub>2</sub>S that colloidal S is formed. In expts. on the reaction of SO<sub>2</sub> and H<sub>2</sub>S in PhMe, in which both are sol., the 2 solns. were mixed rapidly, under which conditions the liquid remained clear (though becoming a progressively deeper yellow) for some time, after which it became turbid and a granular deposit was formed. Evapn. of the clear liquids, before and after the onset of the turbidity and deposition, by the pectographic method of B. (cf. *C. A.* 25, 2622), yielded a viscous oily film, the subsequent behavior of which was followed microscopically for 10 days. This liquid gradually crystd. in a very characteristic way, which is described and illustrated by photomicrographs. The phenomenon probably depends upon the formation of colloidal S in a highly dispersed form in phys. and chem. combination with the water formed in the reaction, then coagulation to amorphous S (with loss of water, corresponding to the formation of a jelly) and finally the formation of crystd. S from amorphous S (formation of solid from jelly). The reaction in rubber is probably like that in PhMe, so that vulcanization with SO<sub>2</sub> and H<sub>2</sub>S depends upon the high state of dispersion of the S and not upon its colloidal state.

C. C. DAVIS

**Isoprene and rubber.** XXXIV. **Molecules or micelles in a rubber solution.** H. STAUDINGER AND H. F. BONDY WITH J. JOSEPH AND E. O. LEUPOLD. *Ann.* 488, 127-53 (1931); cf. *C. A.* 25, 5055; Leupold, *Diss.* Freiburg 1931.—Following a discussion of earlier views on the structure of the colloidal particles in a rubber soln., of polystyrene as a model of rubber, and of viscosity measurements of rubber soln., expts. deal with deviations from the Hagen-Poiseuille law, the behavior of a rubber soln. exposed to light and agitated, the behavior of rubber solns. when heated, their behavior toward O, mol.-wt. detns. of rubber and a comparison of crude, purified and synthetic rubber and latex as an emulloid. Viscosity measurements of 60 solns. of rubbers of different av. mol. wts. (10,000-225,000) showed that with low-mol. rubber (below 40,000) only slight macromol. viscosity phenomena appear, and that only with rubbers of mol. wts. of 100,000-200,000 are the phenomena of significance. The more dil. the solns. the less is the deviation from the Hagen-Poiseuille law, and therefore to det. the highest mol. wts. from viscosity detns. very dil. solns. must be used. This influence can be neglected with mol. wts. of 40,000 or less. The diminution in the viscosity of pure rubber solns. when agitated is a result of decompr. by atm. O, for when air-free tetralin solns. of rubber are agitated in the absence of air, there is little or no diminution. When the same tetralin solns. were heated 100 hrs. at 60° in N, the viscosities diminished greatly, and the higher the mol. wt. the greater the diminution, so that rubbers with original mol. wts. of 200,000 and 100,000 had the same mol. wt. after treatment. When tetralin solns. of rubber were agitated in O, air and N, the greatest diminution of viscosity occurred in O, and relatively little in N. Heat accelerated this diminution. It also required far longer agitation in the absence than in the presence of O to dissolve the rubber. Pure rubber solns. are far more sensitive to decompr. by O than are solns. of pale crepe, Para, etc., because of the natural anticatalysts in these crude rubbers. Synthetic rubber is also relatively sensitive to attack by O. Viscosity detns. of lattices which yielded rubbers of different solubilities showed no relation between viscosity and mol. structure and therefore mol. wt. XXXV. **Soluble and insoluble rubber and the fractionation of rubber.** H. STAUDINGER AND H. F.

**BONDY.** *Ibid* 153-75.—A crit. review and discussion of the properties of sol. and insol. rubber and the transformation of the former into the latter are followed by expts. on the fractionation of rubber under various conditions. On the assumption that sol. rubber is a mixt. of homologous polyrenes, the fractional soln. pptn. method was used, with detns. of the relative viscosities at equal concns., a method already used for other hydrocarbons (cf. *C. A.* 21, 1271). Rubber purified by the method of Pummerer, Andriesen and Gündel (*C. A.* 22, 4873) was fractionally extd. in  $\text{CO}_2$  with  $\text{Et}_2\text{O}$ ; after all  $\text{Et}_2\text{O}$ -sol. rubber was removed  $\text{EtBr}$  was added to the  $\text{Et}_2\text{O}$  until all rubber dissolved; the solvent was evapd. *in vacuo*, and the individual fractions were thus obtained. The lower fractions were sol. in  $\text{C}_6\text{H}_6$ , and the higher fractions were insol. because of transformation to this state. Prolonged agitation in  $\text{PhBr}$  in the light dissolved all fractions, and the viscosities of all fractions were nearly the same in this solvent. That soln. in  $\text{PbBr}$  involves an irreversible decompn. and not a disaggregation of micelles was proved by viscosity detns. at different temps. The sp. viscosity of  $\text{C}_6\text{H}_6$  solns. of rubber was lower at  $60^\circ$  than at  $20^\circ$ , but increased to its original value on cooling to  $20^\circ$ . In  $\text{PhBr}$ , however, the diminution caused by heating was permanent; so here an irreversible mol. decompn. occurred. Fractionation of purified rubber in the cold in turn by  $\text{Et}_2\text{O}$  and  $\text{C}_6\text{H}_6$  again gave viscosity values which with the low fractions increased in the expected way, but with the later fractions diminished greatly until with the last few fractions the values remained const. O was excluded, and this phenomenon is unexplained, unless traces of O in the original substances were responsible. Fractionation in darkness with the greatest possible exclusion of O and in the cold gave viscosity values in tetralin which showed that the most difficultly sol. fractions have the highest mol. wts., as with polystyrene. Rubber fractions of different av. mol. wts. were kept in tetralin in an abs. vacuum in darkness for 1 month, and the viscosities were detd. periodically. No change occurred with the lowest-mol. rubbers, whereas with the higher-mol. rubbers the viscosity diminished (probably because of contact with O during sampling). After 6 months all fractions were almost completely transformed into insol. rubber. This transformation was most rapid with the highest-mol. fractions. All these insol. products dissolved in tetralin with  $\text{CH}_3\text{CICO}_2\text{H}$  (0.01 mol. per isoprene unit) when agitated for 1 day, or when heated at  $60^\circ$  in tetralin in the presence of air for 1-2 weeks. The viscosities of all these solns. were low, and the rubbers had av. mol. wts. of 15,000-20,000 and a degree of polymerization of approx. 200. C. C. D.

**Substitutes for crude rubber.** HENRY P. STEVENS. *Rubber Age* (N. Y.) 29, 411-2 (1931).—See *C. A.* 25, 2876. C. C. DAVIS

**Several procedures for the preparation of recent vulcanization accelerators.** RUDOLF DITMAR. *Kolloid-Z.* 56, 248-51 (1931). A. FLEISCHER

**Color reactions of latex as a mark of identification of Hevea clones.** W. BOBILIOFF. *Arch. Rubbervelt* 15, 289-301 (1931) (in English 302-8).—The expts. are a continuation of earlier work (cf. *Arch. Rubbervelt* 8, 817 (1924)). The enzymes are activated by Ca and Mg salts, and this activity is manifest as a discoloration of the latex and of the serum. The best results were obtained with 1%  $\text{CaCl}_2$ . The discoloration is a fairly const. and characteristic property of trees, and can be utilized in identifying clones. The reaction should be carried out with a few drops of latex from the leaves under controlled conditions. Only latex from young leaves and from green young bark gives the reaction. The results of various clones are described. C. C. DAVIS

**Physicochemical constitution of certain rubber latex.** F. HEIM DE BALSAC. *Bull. agr. Congo Belge* 21, 1145-51 (1930).—Agglutinating and coagulating powers are suggested as criteria for comparing the action of different coagulating agents. The power of agglutination is a function of the quantity of the substance necessary to form the first flocks in the latex, and the coagulation power is a function of the quantity of the substance necessary to det. the structure of the curd. Two essential factors which det. the stability of the latex are the surface tension and the elec. charge of the globules. The agglutinating and coagulating powers of mineral acids and electrolytes depend on the H-ion concn. The coagulating action of nonelectrolytes is proportional to the intensity of their adsorption on the surface of the globules. An explanation is given for the reticular structure of the curd. J. R. ADAMS

**The chemistry of latex. IV. Specific gravity and crepe content of Hevea latex in relation to the influence of the non-crepe components.** PAUL SCHOLZ AND KARL KLOTZ. *Kautschuk* 7, 142-5 (1931); cf. *C. A.* 25, 4437.—The d. and crepe contents (precise to 0.02% and  $\pm 0.2\%$ , resp.) of 91 samples of latex were detd., and with 85 of the samples the total solids and from this the non-crepe components were also detd., with the object of establishing relations between d., crepe content and non-crepe components.

The results are shown graphically. The "middle line" of all the d-crepe content points lay in a position which corresponded according to the law of mixts. to a d. of 1.023 of the dispersing agent and of 0.901 of the dispersed phase (rubber?). The individual values were so widely scattered, however, that with a given d., they deviated on both sides of the middle line to an extent which corresponded to 3% crepe content. An indirect detn. of the crepe content by a detn. of the d., and with use of the d-crepe content line, is therefore impossible if precise results are desired. With the same crepe content, the d. of the latex depends upon the non-crepe components, for with a given crepe content the higher the content of the non-crepe components the higher is the d. of the latex. The diminishing content of non-crepe components which accompanies an increase in crepe content is responsible for the declining course of the d-crepe content middle line, and the scattering of the individual points is also influenced by the content of non-crepe components.

C. C. DAVIS

**The concentration of rubber latex and latex mixtures.** D. F. TWISS. *Rev. gén. caoutchouc* 8, No. 72, 16-21(1931); cf. *C. A.* 25, 4737.—An illustrated review and discussion.

C. C. DAVIS

**Patents on the electrophoresis of rubber latex.** RUDOLF DITMAR. *Caoutchouc & gutta-percha* 28, 15691-3(1931).—A review and discussion.

C. C. DAVIS

**Latex as a bonding agent in brake linings.** JOHN A. LUNN. *Rubber Age* (N. Y.) 29, 413-5(1931).—An illustrated review and discussion. It has been found that the ideal binder should (1) have a high tensile strength; (2) have uniform distribution; (3) have uniform friction at all temps. and humidities; (4) be noiseless; (5) have a low wear factor; (6) not cause scoring; (7) not bleed at high temps. and pressures; (8) not swell at high temps. and cause binding or destruction of the bond; (9) be of such a nature that its phys. and chem. properties can be controlled in manuf.; (10) have good aging properties. Brake linings made with a rubber binder for the asbestos are particularly satisfactory in conforming to these desiderata.

C. C. DAVIS

**Experiments on the autoxidation of rubber and the catalytic phenomena which are associated with it.** CHARLES DUFRAISSE AND NICOLAS DRISCH. *Rev. gén. caoutchouc* 8, No. 71, 9-24(1931).—A study of the rate of absorption of O by rubber under various conditions, and different factors which influence the rate, including  $\text{Me}_2\text{CO}$  extn. before and after vulcanization,  $\text{Me}_2\text{CO}$ -sol. resin, free S, org. accelerators and com. anti-oxygens. The method was essentially that used by Moureu, D. and their collaborators for studying autoxidation, in general, with addn. of the various protective agents by the diffusion method of Moureu, D. and Lotte (*C. A.* 24, 3396, 4959). Special attention was paid to the beginning of oxidation, *i. e.*, when less than 1% O (0.02 mol. per isoprene unit) had reacted. The sensitivity of the method made possible the detection of oxidative changes when only 1 part of O per 10,000 parts of rubber had reacted. Raw rubber extd. with AcMe oxidized at its original rate after the natural protective agents (removed by AcMe) were restored. In general, raw rubber showed changes when it had absorbed 0.4% O and vulcanized rubber when 0.6% had been absorbed. Pale crepe extn. with AcMe in a Soxhlet yielded 0.5% of a cryst. substance which had no protective action against aging, and 1.8% of a resin which, by tests in its presence and absence, was shown to be the chief cause of the stability of raw rubber toward O (cf. Bruson, Sebrell and Vogt, *C. A.* 21, 4095-6). The protective action of this resin is not wholly destroyed during vulcanization, for rubber-S vulcanizates became still more sensitive to oxidation when extd. with AcMe, and the addn. of the same quantity of fresh resin restored the original stability. The natural protective substances of raw rubber did not, however, protect vulcanized rubber so effectively, and therefore the ultimate detn. of their compn. may not after all be of great practical value. Since the same agents are not correspondingly effective in raw and vulcanized rubber, the sensitivity of rubber to oxidation depends upon its chem. state. The resin did not lose its protective power when heated in air at 127° for 9 hrs., so that its alteration during vulcanization is not from heat. The resin was also a good protective agent for limonene and pinene. Systematic tests of vulcanizates extd. and unextd. with  $\text{Me}_2\text{CO}$  and with and without free S, *e. g.*, vulcanizates extd. and unextd. with  $\text{Me}_2\text{CO}$  and prep'd. from  $\text{Me}_2\text{CO}$ -extd. rubber, showed that free S has no appreciable influence on the sensitivity of vulcanized rubber to oxidation. When rubber-S vulcanizates, extd. and unextd. with  $\text{Me}_2\text{CO}$ , were treated with various com. accelerators, considerable differences were found in the rates of oxidation under different conditions with the individual accelerators. Toward limonene,  $\alpha$ -pinene, styrolene and  $\text{BzH}$ , the accelerators behaved in different ways in each case (accelerated oxidation occurring in 1 case), and, in general, the protective action of rubber accelerators varies greatly toward different oxidizable compds. Further tests show the relative protective action of com.

protective agents and the  $\text{Me}_2\text{CO}$  ext. of rubber on vulcanized rubber. There was an induction period in the various oxidations, as found by previous experimenters.

C. C. DAVIS

**The nerve of rubber.** J. BEHRE. *Kautschuk* 7, 161-5(1931).—A comparison of Traube's stalagmetric measurements (cf. Freundlich, *Kapillarchemie*, 3rd Ed., 31) and of the capillary measurements by the method of Greinert and B. (cf. *C. A.* 20, 1729) showed a linear relation between the 2 properties, and this proves in turn that in the capillary method surface tension and not the viscosity of the soln. is measured. A comparison of the surface tensions of rubber solns. with the surface tensions of the corresponding solid rubbers (detd. by Berggren, cf. *C. A.* 8, 2287) then showed a linear relation between these 2 properties. Since the Traube, Berggren and capillary methods are linear functions of one another, the capillary method measures the nerve of the rubber. The relation between this nerve and the phys. properties of rubber-S vulcanizates was then studied with a wide variety of rubbers masticated to various degrees. There was a direct relation between the nerve of a raw rubber and its tensile strength when vulcanized, so that the capillary method is a criterion of the tensile strength and of a rubber. The ratio: tensile strength/nerve varied among different types of rubbers, e. g., for the same nerve values light brown crepe and sprayed rubber had higher tensile strengths than those of 1st latex crepe and smoked sheet.

C. C. DAVIS

**Rubber molecule or rubber micelles.** H. KROEPELIN. *Rev. gén. caoutchouc* 8, No. 72, 23-4(1931); cf. *C. A.* 24, 4954.—In dil. soln. rubber might exist in 3 forms: (1) individual independent mols.; (2) micelles (aggregates) of different sizes in equil. with individual mols.; or (3) assocns. of mols. with a certain cohesion, which are not destroyed by diln. and which are formed of the same mols. An array of exptl. facts from the work of various investigators is given as evidence that the 3rd hypothesis is the most probable.

C. C. DAVIS

**Recent developments in the field of microscopy, with special reference to their technical application to rubber.** E. A. HAUSER. *Kautschuk* 7, 168-9(1931); cf. *C. A.* 25, 4152.—A review and discussion.

C. C. DAVIS

**Microporous rubber, its preparation, properties and use.** H. BECKMANN. *Kautschuk* 7, 149-55(1931).—A review and discussion of the work of B., which is covered by numerous patents.

C. C. DAVIS

**Very active rubber fillers.** RUDOLF DITMAR. *Caoutchouc & gutta-percha* 28, 15680-1(1931).—A discussion of several recently patented products.

C. C. DAVIS

**New condensation products of rubber hydrocarbons obtained by means of benzyl chloride.** F. KIRCHHOF. *Kautschuk* 7, 128-32(1931).—The application of the Friedel-Crafts reaction to rubber hydrocarbons forms a new type of condensation products which may be regarded provisionally as aracyclorubbers (benzylidene rubbers) since benzylidene groups are probably condensed with the polyprene skeleton to form cyclic systems. The products are white to yellowish amorphous substances which contain only C and H. In phys. and chem. properties they resemble the already known polybenzylidene ( $\text{C}_7\text{H}_6$ )<sub>2</sub>. Anhyd.  $\text{AlCl}_3$  suspended in  $\text{CCl}_4$ , added rapidly to cold rubber and  $\text{PhCH}_2\text{Cl}$  in  $\text{CCl}_4$ , results in an energetic reaction, with evolution of  $\text{HCl}$  and formation of a gray-white spongy mass, which, after completion of the reaction on a boiling water bath, evapn. and extn. with  $\text{AcMe}$ , is a brittle amorphous product. If, on the other hand,  $\text{PhCH}_2\text{Cl}$  is added dropwise to rubber and  $\text{PhCH}_2\text{Cl}$  in  $\text{CCl}_4$  contg.  $\text{AlCl}_3$  in suspension, a red-brown mass is obtained. When the reaction mixt. is cooled there seps. a hard mass, which, extd. with  $\text{AcMe}$ , yields a yellow-brown powder with all the properties of the cyclorubber of Bruson (cf. *C. A.* 21, 3486). The yield of these products depends greatly upon the concn. of the rubber soln. and its degree of depolymerization. Relatively small quantities of  $\text{AcMe}$ - and  $\text{C}_6\text{H}_6$ -sol. yellow resins are also formed, the yields of which depend upon the temp. and the proportion of  $\text{AlCl}_3$ . They were not studied further except to find that they showed weak fluorescence in ultra-violet light. The benzylidene rubbers are white to pale yellowish amorphous substances which are pulverized with extreme ease. Their d. is about 1.10, and they barely swell in org. solvents. They were thermoplastic above 100°. Purified by extn. with  $\text{AcMe}$ , they still contain 0.5-3.0% org. Cl which is removed by boiling  $\text{PhNH}_2$ . They are very inactive toward O and halogens, though on prolonged contact with Br in  $\text{CCl}_4$  there is some substitution. They sinter around 180°, and form at higher temps. a porous coal-like substance. In ultra-violet light they showed bright violet fluorescence, whereas the cyclorubber of Bruson was a pale yellow-brown. The benzylidene rubbers were not a mixt. of this cyclorubber and the ( $\text{C}_7\text{H}_6$ )<sub>2</sub> formed from  $\text{PhCH}_2\text{Cl}$  and  $\text{AlCl}_3$  (cf. *Ber.* 27, 3237), because with concd.  $\text{H}_2\text{SO}_4$  at 280° and with boiling  $\text{CCl}_4$ ,

$\text{CO}_2\text{H}$  the characteristic reaction of the cyclorubber did not occur. Because of the high polymeric amorphous nature of the benzylidene rubbers their constitution could not be established. Analysis showed in one case the empirical formula  $(\text{C}_{26}\text{H}_{36})_n$ . As a beginning toward an explanation, a theory of the formation of  $(\text{C}_7\text{H}_8)_n$  is suggested and it is shown that an analogous series of reactions may take place in the formation of benzylidene rubbers.

C. C. DAVIS

**The effect of maturation on the plasticity of smoked sheet.** G. MARTIN AND L. E. ELLIOTT. *Trop. Agr.* (Ceylon) 76, 345-9 (1931).—Exptl. results on 2 sets of sheet samples show that keeping the coagulum in the serum has no definite effect on the hardness of the sheet samples, even after storage for 6 months under different conditions. Keeping the coagulum in the serum for 44 hrs. instead of 4 hrs. reduced the time of vulcanization by 15% in the absence of *p*-nitrophenol and by 8% in its presence.

JOHN O. HARDESTY

**The plasticization of rubber.** F. JACOBS. *Rev. gén. caoutchouc* 8, No. 71, 31-8 (1931); cf. *C. A.* 25, 3870.—The manuf. and properties of stearic acid and the behavior of com. grades in rubber are reviewed and discussed.

C. C. DAVIS

**The effect of blanketing on the plasticity of crepe.** G. MARTIN AND L. E. ELLIOTT. *Trop. Agr.* (Ceylon) 76, 274-5 (1931).—Blanketing has little effect on plasticity of crepe when the temp. of the rolls is kept low, but it may have a marked effect if the rolls become hot. To obtain rubber of uniform plasticity it is desirable that the blanketing rolls be water-cooled.

JOHN O. HARDESTY

**The use of titanic acid as a regulator of the reaction in the manufacture of "Radifix" [rapeseed oil factice].** RUDOLF DITMAR. *Caoutchouc & gutta-percha* 28, 15684 (1931).—When  $\text{TiO}_2$  is added to the mixt. of oil, kieselguhr and  $\text{CCl}_4$ , it retards the reaction and prevents sponging upon the addn. of the  $\text{CCl}_4$  soln. of  $\text{S}_2\text{Cl}_2$ . The procedure recommended is to add a mixt. of  $\text{S}_2\text{Cl}_2$  7 parts in  $\text{CCl}_4$  to a mixt. of rapeseed oil 20, kieselguhr 10,  $\text{TiO}_2$  10 and  $\text{CCl}_4$  10.

C. C. DAVIS

**Making rubber thread.** JOSEPH ROSSMAN. *India Rubber World* 85, No. 1, 59-60 (1931).—A survey of U. S. patents.

C. C. DAVIS

**Determination of sulfur in rubber goods and in factice.** M. SAGAJLO, J. BOBIŃSKA AND A. PIKULSKI. *Roczniki Chem.* 11, 289-300 (1931) (300 in French).—A new procedure is proposed for the detn. of total S in rubber products and in factice. Heat 0.5-1 g. of the substance with 1 g. of  $\text{MgO}$  and approx. 10 cc. of  $\text{HNO}_3$  (d. 1.4) until the rubber melts, add approx. 10 cc. of  $\text{HNO}_3$  (d. 1.5), heat 10-15 min., add 15-20 cc. of 20%  $\text{HClO}_4$  and heat the mixt. until the ingredients go into soln. to a clear liquid. Sometimes, especially when factice is analyzed,  $\text{HClO}_4$  must be added several times. Evap. the clear soln. to dryness, heat the residue until all nitric fumes are expelled, cool, dissolve the residue in dil.  $\text{HCl}$  (1:6), filter and det. the S as  $\text{BaSO}_4$ . To det. free S in rubber ext. with acetone, evap., add to the residue 200 cc. of Br water, add 6 cc. of free Br, heat on a water bath until the water layer is clear and on the bottom a yellow or brown oil seps., add 0.5-1 cc. of  $\text{HCl}$ , filter the oil off and det. the S in the filtrate as  $\text{BaSO}_4$ . S in the oil is detd. by the  $\text{HClO}_4$  method; it represents S combined with resins in the substance analyzed.

J. WIERTELAK

**Toxic substances in the rubber industry.** XXI. *p*-Nitrosodimethylaniline. P. A. DAVIS. *Rubber Age* (N. Y.) 29, 367-8 (1931); cf. *C. A.* 25, 3197.—The high toxicity of  $p\text{-ONC}_6\text{H}_4\text{NMe}_2$ , which leads to dermatitis, conjunctivitis, coryza, rhinitis, bronchitis, gastritis, enterocolitis, nephritis and toxic anemia, means that the greatest care should be exercised. Treatments for the various conditions mentioned above are also described. XXII. *Ibid.* 461-2.—Com. phenyl- $\beta$ -naphthylamine contains impurities and also forms thio compds. during vulcanization, but because of the small proportions used in rubber these impurities and decompn. products are in insufficient quantities to cause trouble. Expts. with guinea pigs and with human beings and experience with workers show that phenyl- $\beta$ -naphthylamine is not dangerous when used with care during manuf., but that some individuals (approx. 3%) are hypersensitive either directly or after continued exposure, and that this substance should not be used in rubber products which come in contact with the skin. This contact effect is true above all when the phenyl- $\beta$ -naphthylamine has bloomed to the surface of the rubber. Those with hyperthyroid secretion, a high basal metabolism rate, a high  $p_K$  value of the blood or a disturbed endocrine balance should not be exposed.

C. C. DAVIS

**Value of rubber hydrocarbon in reclaimed rubber.** C. W. SANDERSON. *Ind. Eng. Chem.* 23, 989-91 (1931).—The rubber hydrocarbon of a whole-tire alkali-reclaimed rubber was evaluated in the same way as in previous expts. (cf. *C. A.* 23, 4099) in a series of vulcanizates of const. ultimate compn. based on analysis (cf. Vogt, *C. A.* 22, 1058). Under these conditions the reclaimed rubber hydrocarbon had a max. value

in the vulcanizate contg. no new rubber, where the resistance to abrasion was about 0.5 as great as that of the vulcanizate contg. no reclaimed rubber. It is impracticable to compensate for the inferior effect of the reclaimed rubber because any method could also be utilized for the improvement of the corresponding vulcanizate contg. no reclaimed rubber.

C. C. DAVIS

**Reclaimed rubber.** A. T. MCPHERSON. U. S. Bur. Standards, *Circ.* No. 393, 1-22(1931).—A review and description of current practice in the manuf. of reclaimed rubbers, and their classification, properties and uses.

C. C. DAVIS

**Accelerators of vulcanization.** F. JACOBS. *Caoutchouc & gutta-percha* 28, 15674-9 (1931); cf. *C. A.* 25, 5595.—The general properties and behavior in rubber of "Vulcamel" (a condensation product of butyraldehyde and NH<sub>3</sub>) and furfuranimide are described, with quant. data.

C. C. DAVIS

**The use of accelerators and of protective agents against aging [of rubber].** ARNOLD H. SMITH. *Kautschuk* 7, 70-5(1931).—A review and discussion of present-day practice.

C. C. DAVIS

**Piperidine accelerators.** P. SCHIDROWITZ. *India Rubber J.* 82, 25-6, 28-30 (1931).—The expts. show the comparative activity and behavior of piperidine pentamethylenedithiocarbamate (I), Zn pentamethylenedithiocarbamate (II) and Pb pentamethylenedithiocarbamate (III) in the mixt.: pale crepe 100, S 0.75-3, accelerator 0.1-1, stearic acid 0.5, ZnO 2.5, with the results in graphical form. With I, the best quality was obtained with 2% S and 0.35% I. The quality was also good with 0.75% S and 1% I, in which more S increased the stiffness but not the tensile strength. With II, 1.25% S is necessary with 1% II, while with 2% S the quality improves up to 1% II. With III, 1.2% S is necessary with 1% III, while with 2% S, 0.35% III gives the best quality, in which the modulus is greater than with II. In general, I is the most powerful accelerator and II the weakest one. With mixts. which gave equiv. technical cures (2% S, and 0.25% I, 0.5% II, 0.5% III, resp.), the tendency to bring about "scorching" and "setting up" was by far the greatest with I, while II and III were similar. Further tests show that Zn diethyldithiocarbamate and Zn dimethylidithiocarbamate are similar to II in their general behavior as accelerators, while dinitrophenyldimethylidithiocarbamate is similar to III. PbO activates the accelerating action of III. The curves were at different temps.

C. C. DAVIS

**The luminescence of accelerators and of preservative agents most used in the rubber industry.** RUDOLPH DITMAR. *Caoutchouc & gutta-percha* 28, 15685-6(1931).—With the same method used by Kirchhof (cf. *C. A.* 22, 2291, 2855) and by D. and Dietsch (*C. A.* 22, 3317) the luminescences in ultra-violet light of various com. important org. accelerators and protective agents were detd. The method serves to control com. grades, for the color of the same product, e. g., mercaptobenzothiazole, varies with the manufacturer.

C. C. DAVIS

**The vulcanization problem. Its scientific aspect at the present day.** E. LINDMAYER. *India Rubber J.* 82, 218-22, 249-51(1931).—A review and discussion of present-day knowledge indicates that the primary reaction in vulcanization is chem. or phys.-chem., i. e., the vulcanizing agent enters between 2CH<sub>2</sub> groups or links the terminal valences. This reaction takes place without change of temp., forms soft vulcanized rubber which is reclaimable, and does not modify the internal structure. It does, however, explain insol., increased resistance to deformation, greater elasticity and insensitivity to change in temp. It is accelerated by org. and inorg. catalysts and by ultra-violet radiation. The secondary reaction involves satn., accompanied by substitution and partial decomprn. The latter explains the low resistance of leathery partially vulcanized hard rubber, and the transitory diminution in dielec. power. Complete topographic deformation of the mols. leads to hard rubber, which cannot be reclaimed. This reaction is similar to oxidation, halogenation and hydrogenation. It is exothermic and the effect of accelerators is relatively small.

C. C. DAVIS

**Manifold press vulcanizer.** P. E. WELTON. *India Rubber World* 85, No. 1, 56 (1931).—An illustrated description of a new type of equipment.

C. C. DAVIS

## Patents

**Rubber.** "HEROLD" A.-G. Ger. 527,888, Aug. 29, 1928. A vulcanizing mold for rubber is coated on the inner side with water glass, which is, in turn, coated with sugar soln. Dextrin, maltose, grape, cane, beet or crude sugar may be used.

**Treatment of rubber.** WILLIAM S. CALCOTT and WILLIAM A. DOUGLASS (to E. I. du Pont de Nemours and Co.). Can. 313,988, Aug. 4, 1931. *p*-PhC<sub>6</sub>H<sub>4</sub>OH is incor-

porated with a rubber mix and vulcanized to resist deterioration and oxidation of the rubber.

**Preserving rubber latex.** I. G. FARBENIND. A.-G. (Kurt H. Meyer and Friedrich Hopff, inventors). Ger. 530,434, May 29, 1926. The latex is treated with a small quantity of a water-sol. aliphatic, aromatic or hydroaromatic amine.  $\text{MeNH}_2$ ,  $\text{EtNH}_2$ ,  $\text{PhCH}_2\text{NH}_2$ , cyclohexylamine and piperidine are suitable.

**Rubber dispersions.** SOCIETÀ ITALIANA PIRELLI and UGO PESTALOZZA. Fr. 705,207, Nov. 6, 1930. Aq. dispersions of rubber are concd. by passing the dispersion backward and forward over cylindrical porous filtering members.

**Colloidal dispersions of rubber and similar materials.** ERNST A. HAUSER and REGINALD H. WATTS (to Dewey and Almy Chemical Co.). U. S. 1,814,473, July 14. In forming rubber casts, etc., a mold form is immersed in a thixotropic aq. dispersion of material such as rubber and the dispersion is allowed to assume the gel condition in contact with the mold-form surface. The mold form and adherent layer of thixotropic gel is then withdrawn from the surrounding dispersion, and the aq. dispersion medium is removed.

**Treatment of pigments to facilitate dispersion.** HERBERT A. ENDRES (to The Goodyear Tire and Rubber Co.). Can. 314,017, Aug. 4, 1931. Pigments for use in compounding rubber are manufd. by adding a soln. of sol. sulfate to a soln. of sol. Ba salt to form a ppt. The ppt. is flocculated by the addn. of a sol. soap of oleic, stearic, palmitic or lauric acid, washed to remove sol. salts and subsequently a sufficient quantity of one of the previously mentioned soaps is added to cause redispersion of the ppt.

**Antioxidant for rubber.** ALBERT M. CLIFFORD (to The Goodyear Tire and Rubber Co.). Can. 314,009, Aug. 4, 1931. Rubber is vulcanized in the presence of  $\beta$ -naphthyl-piperidine to retard oxidation. Cf. C. A. 25, 4442.

**Inhibiting deterioration of rubber.** ALBERT M. CLIFFORD (to Goodyear Tire & Rubber Co.). U. S. 1,813,609, July 7. A naphthyl-substituted benzidine such as di- $\beta$ -naphthyl-substituted benzidine is added.

**Cutting sponge rubber.** WALDEMAR VERNET (to Rubbersan Products, Inc.). U. S. 1,814,197, July 14. App. and various details of operation are described.

**Device for cutting rubber tubes on a mandrel.** GEORGE J. MEAD (to Fisk Rubber Co.). U. S. 1,813,246, July 7. Structural features.

**Tire bead manufacture.** CHARLES W. LEGUILLOON (to B. F. Goodrich Co.). U. S. 1,813,176, July 7. For manuf. of an inextensible tire bead, the surface of a clean steel wire is coated with a film of a tacky heat-plastic rubber isomer, the wire is formed into a multi-strand bead core, the core is surrounded with a vulcanizable rubber compn. and the materials are heated to a vulcanizing temp. so that the outer portion of the bead is bonded to the wire core through the rubber isomer, in a permanent bond.

**Protective rubber coatings on articles such as sheet steel.** BENTON DALES (to B. F. Goodrich Co.). U. S. 1,813,440, July 7. A layer of rubber isomer is deposited on the article from a liquid dispersion, followed by deposition of a layer of rubber from an aq. dispersion and drying of the deposited layers, which may then be vulcanized.

**Synthetic rubber.** HANS TOCHTERMANN and CLAUS HEUCK (to I. G. Farbenind. A.-G.). U. S. 1,814,420, July 14. For prep. material against "ageing," aldol- $\alpha$ -naphthylamine in an emulsified state is mixed with a product prep'd. by polymerizing isoprene in the form of an emulsion and coagulating.

**Synthetic rubber.** CHEMISCHE FABRIKEN KURT ALBERT G. M. B. H. Fr. 705,069, Oct. 28, 1930. Rubber-like masses are prep'd. by heating to reaction temp. a mixt. of castor oil, a polyhydric alc. with more than 2OH groups and a dibasic aliphatic acid contg. 6-10C atoms. A drying oil such as linseed oil may be added before, during or after the condensation. An example is given in which a mixt. of sebacic acid, castor oil, glycerol and crude linseed oil is heated to 185-195°.

**Rubber substitutes.** JEAN BAER. Ger. 530,163, Apr. 24, 1928. An aliphatic aldehyde, particularly  $\text{CH}_2\text{O}$ , or a mixt. thereof, with a dihalogenated satd. hydrocarbon, e. g.,  $\text{CH}_2\text{Br}_2$  or  $\text{C}_2\text{H}_4\text{Cl}_2$ , is treated at atm. temp. or in the warm with a soln. of an alkali-metal or alk. earth polysulfide. Examples are given. Cf. C. A. 25, 2332.

**Gutta-percha, etc.** WILLOUGHBY S. SMITH, HENRY J. GARNETT and JOHN N. DEAN. Fr. 705,291, Nov. 8, 1930. Gutta-percha, balata, etc., are refined by treating the crude material with a solvent having a selective action of such a nature or used under such conditions that the gutta-percha, etc., of high quality swells at most, while the gutta-percha of poorer quality is dissolved, then sepg. the solvent from the residue. Suitable solvents include  $\text{C}_6\text{H}_6$  and its homologs, petr. ether and ethyl acetate. The purified products are used for elec. insulators. Cf. C. A. 25, 4150.

**Molding and vulcanizing rubber articles such as shoe soles.** ERNEST W. DUNBAR (to Cambridge Rubber Co.). U. S. 1,813,235, July 7. Mech. features.

**Anti-aging compounds for use in the vulcanizing of rubber.** THE RUBBER SERVICE LABORATORIES Co. Fr. 705,158, Nov. 5, 1930. A hydroxyaryl sulfide such as dihydroxydinaphthyl sulfide and an aryl amine such as  $\text{PhNH}_2$  are condensed, preferably in the proportion of 1 gram mol. of sulfide to 2 of amine. Examples are given.

**Rubber vulcanization control.** SIDNEY M. CADWELL (to Naugatuck Chemical Co.). U. S. 1,814,286, July 14. For controlling the vulcanization of rubber contg. S, an amine such as aniline or diethylamine, a metal compd. such as  $\text{ZnO}$  and a material contg.  $\text{CS}_2$  such as hydroxybutylthiocarbonic acid disulfide, the amine contained in the rubber is caused to react with an aldehyde such as benzaldehyde to check the usual vulcanizing action on the rubber of the amine, the rubber is treated with a quantity of amine and the vulcanization is effected. U. S. 1,814,287 relates to control of vulcanization of rubber contg. S, an amine, a metal compd. such as  $\text{ZnO}$  and  $\text{CS}_2$  or other substance contg. the group X:CS (in which X is S or an equiv. element or group) by causing the amine contained in the rubber to react with a nitroso compd. such as *p*-nitrosodimethylaniline to check the usual vulcanizing action on the rubber, treating the rubber with a quantity of amine and vulcanizing. U. S. 1,814,288 specifies vulcanization control by the reaction upon an active metal such as Zn in combination such as  $\text{ZnO}$  in the presence of an amine with a material contg. the group X:CS and with a substance such as  $\text{H}_2\text{S}$  to check the vulcanizing action of the active metal in combination.

**Centrifugal concentration of latex.** CHAUNCEY C. LOOMIS and HORACE E. STUMP (to U. S. Rubber Co.). U. S. 1,816,018, July 28. Latex is treated with an alkali and a protective colloid and centrifuged, and a concd. thick creamy uncoagulated water-dispersible product is sepd.

**Purifying latex emulsions.** WM. B. WESCOTT (to Rubber Latex Research Corp.). U. S. 1,816,242, July 28. A continuously moving stream of latex is subjected to a progressively increasing centrifugal force without violent agitation of the latex, an inner liquid layer enriched in emulsiform rubber-forming particles is sepd., the natural serum of the layer is replaced with water and a protective ingredient such as  $\text{NH}_3$  or borax, and the enriched and washed layer is removed from the influence of centrifugal force without violent agitation and as an effluent with a progressively decreased velocity to preserve the natural condition of the rubber-forming particles. Cf. C. A. 24, 2915.

**Homogeneous rubber deposits from rubber latex.** FRANCIS GABOR, PAUL KLEIN and ANDREW SZEGVARI (to American Anode, Inc.). U. S. 1,815,057, July 21. For making homogeneous rubber deposits from ammonia-preserved latex by electrophoretic deposition, the  $\text{NH}_3$  content of the latex is reduced by adding substances such as formaldehyde and there is immersed in the treated latex a deposition base comprising a metal such as Zn, Cd, Fe or Pb substantially incapable under the influence of an electrophoretic depositing current of forming gases on its surface, and deposition is effected by an elec. current.

**Concentrating aqueous dispersions of rubber.** SOC. ITALIANA PIRELLI and U. PESTALOZZA. Brit. 344,875, Nov. 8, 1929. A filtering medium such as a hollow earthenware filter is arranged in an aq. dispersion of rubber or like material, and relative movement is produced between the liquid and the filter sufficient to maintain the pores of the filter free for the passage of the aq. medium until the dispersion has attained the desired degree of concn. App. is described.

**Rubber composition.** ANSEL M. KINNEY (to Standard Oil Co. of Ind.). U. S. 1,815,778, July 21. A compn. which has good strength and durability is formed from rubber together with vulcanizing ingredients, and preferentially oil-sol. naphthenic acid (derived from mineral oils) in the proportion of 0.5-5% the quantity of the rubber.

**Preserving rubber.** MARION C. REED (to B. F. Goodrich Co.). U. S. 1,815,072, July 21. Rubber is treated with a small proportion (suitably about 0.2-5%) of a primary amino deriv. of a diaryl ether, such as diaminodiphenyl ether.

**Weather-proof protective coating for rubber.** SAMUEL C. WITHERSPOON and ARTHUR F. BEAL. U. S. 1,815,998, July 28. A protective coating compn. suitable for use on rubber comprises nitrocellulose, a larger quantity of paraffin and a still larger quantity of raw rubber, and a small quantity of dye and anti-oxidant, dissolved in a solvent comprising  $\text{AmOAc}$  and benzene.

**Retarding the deterioration of rubber.** LOUIS H. HOWLAND (to The Dominion Rubber Co., Ltd.). Can. 314,590, Aug. 25, 1931. Rubber is treated with methyl-acridine to retard deterioration.

**Rendering rubber resistant to aging.** ALBERT M. CLIFFORD (to Goodyear Tire

& Rubber Co.). U. S. 1,818,942, Aug. 11. Vulcanization is effected in the presence of a reaction product of naphthylamine and formic acid formed in the presence of aniline. Cf. *C. A.* 25, 4443.

**Addition products of naphthols and organic bases.** S. M. CADWELL and S. I. STRICKHOUSER (to Naugatuck Chemical Co.). Brit. 342,502, Jan. 19, 1929. Compds. suitable for addn. to rubber to prevent deterioration are formed by the combination of  $\alpha$ - and  $\beta$ -naphthols and 1,5-dihydroxynaphthalene with various org. bases such as polyethylenepolyamine, diethylenetriamine, pentamethyldiethylenetriamine, ethyl- $\alpha$ -naphthylamine, di- $\alpha$ -naphthylurea, dianisidine, dibenzylaniline, methylbenzylaniline, *m*-nitromethylaniline, dibenzylamine and various aldehyde and nitroso derivs.

**Apparatus for producing cellular rubber containing air under pressure.** STEFANO BATTILANI. U. S. 1,818,372, Aug. 11. Structural and mech. features.

**Rubber sponge.** MOSE E. BLUMENFELD. U. S. 1,816,108, July 28. A cleaning device comprises a rubber-sponge body with spun fibers projecting from its surface.

**Rubber sponge.** YVES CORNIC. U. S. 1,816,764, July 28. See Brit. 314,539 (*C. A.* 24, 1545).

**Sheet-rubber stripper machine.** RICHARD H. COOVERT and LOUIE W. WILKINSON. U. S. 1,818,792, Aug. 11. Mech. features.

**Rubberized material for use as a leather substitute.** HAROLD D. RICE (to Woonsocket Rubber Co.). U. S. 1,817,323, Aug. 4. A bat of fibrous sheet material such as blended rayon, hemp, wool and cotton is impregnated with rubber, a coating of rubber is applied to the sheet, the coating is superficially treated by halogenation, embossed, vulcanized and finally halogenated (suitably with Br and sulfur chloride).

**Insulator containing rubber.** ELECTRICAL RESEARCH PRODUCTS, INC. Fr. 38,129, Mar. 12, 1930. Addn. to 659,750 (*C. A.* 23, 5254). Rubber to be used as an ingredient in insulating materials is purified by submitting it in the form of latex or crude rubber to the action of water contg. about 2% caustic alkali under pressure for 1-8 hrs. The rubber is coagulated by the addn. of AcOH and washed.

**Reducing the tackiness of unvulcanized rubber surfaces.** WILLIS A. GIBBONS (to Morgan & Wright). U. S. 1,817,363, Aug. 4. The surfaces are treated with a "tackiness-reducing" compd. such as ammonium stearate which is decomposable at vulcanizing temps. into portions at least one of which is volatile, and which leaves substantially no deposit on the surface at the termination of the vulcanizing operation.

**Waste rubber.** W. J. CRAYMER. Australia 22,482, Sept. 17, 1929. Waste rubber is disintegrated and treated with a rubber solvent to form a plastic mass. The mass is passed through a mixing machine and formed into sheets by heat and pressure.

**Synthetic rubber.** I. G. FARBEININD. A.-G. Fr. 38,127, Mar. 11, 1930. Addn. to 658,652 (*C. A.* 23, 5352). Rubber-like compds. are prep'd. by polymerizing butadiene hydrocarbons in the presence of solvent or diluent hydrocarbons which have a b. p. above or below that of the butadiene hydrocarbons and which do not take part in the polymerization. Suitable solvents or diluents are amylene, petrol, cyclohexane,  $C_6H_6$ , xylene, turpentine, etc. The amt. of and nature of the solvent or diluent have a great influence on the nature and state of the final product.

**Age-resisting vulcanized rubber.** JOSEPH R. INGRAM (to Rubber Service Laboratories Co.). U. S. 1,816,851, Aug. 4. Before vulcanization with S a rubber compn. has incorporated with it an antioxidant comprising a reaction product of an amino biphenyl such as  $\rho$ -aminobiphenyl and an aryl hydroxide such as  $\beta$ -naphthol. Cf. *C. A.* 25, 3876.

**Rubber vulcanization.** JAN TEPPEMA (to Goodyear Tire & Rubber Co.). U. S. 1,818,934, Aug. 11. An accelerator is used selected from a group of substances including the reaction products of diphenylguanidine with each of the following compds.: 5-chloromercaptobenzothiazole, 6-nitromercaptobenzothiazole and 6-aminomercaptobenzothiazole; also the diethylamine salt of chloromercaptobenzothiazole and the diethylamine salt of 6-aminomercaptobenzothiazole.

**Treating air bags such as those used in vulcanizing tires.** CORNELIS VAN RENNES (to Goodyear Tire & Rubber Co.). U. S. 1,818,937, Aug. 11. A soln. of glycerol extd. from used air bags is injected into air bags to protect their inner surfaces from oxidation.

**Pigment for use with rubber.** ARTHUR B. COWDERY (to Barrett Co.). U. S. 1,820,444, Aug. 25. A coal-tar distn. residue is used having not less than about 40% by wt. of constituents which have been produced *in situ* and are insol. in benzene (the residue having a m. p. of about 105°).

**Drying apparatus for rubberized fabrics, etc.** ROY W. BROWN (to Firestone Tire and Rubber Co.). U. S. 1,819,986, Aug. 18. A device such as an elec. testing app.

is provided for detg. the content of volatilized solvent in the gases passing from the drying chamber. Various details of app. are described.

**Rubber-coating materials such as wood.** BUDD BRONSON (to Ohio Rubber Co.). U. S. 1,819,147, Aug. 18. A layer of metal such as Pb, Zn, Cu, brass or Al is sprayed onto a non-metallic material such as wood and a layer of rubber is then vulcanized onto the layer of metal.

**Chlorinated rubber product for use in plastic compositions, paints and lacquers.** FRANCIS C. DYCHE-TEAGUE. U. S. 1,819,136, Aug. 18. A product forming solns. of low viscosity is obtained by rolling rubber in a mill until it is disintegrated, making a soln. from the disintegrated mass, and passing Cl through the soln.

**Precipitated silica.** JOHN W. CHURCH. U. S. 1,819,356, Aug. 18. A colloidal soln. of silica gel is dehydrated until it will no longer revert to its former gelatinous colloidal form in the presence of water, wet ground, washed and then subjected to a second dehydration. The product is suitable for use in *rubber compns.*

**Porous or microporous articles of vulcanized rubber.** EVELYN W. MADGE (to Dunlop Rubber Co., Ltd.). U. S. 1,819,647, Aug. 18. Porous or microporous articles of vulcanized rubber such as battery separators or filter cones are obtained from aq. dispersions without the use of electrolytes or gelling by sepg. the dispersed rubber material from a dispersing medium by electrophoresis and vulcanizing the deposit while preventing the evapn. of liquid from the pores.

**Rubber vulcanization accelerator.** CHARLES J. ROMIEUX and LUDWIG J. CHRISTMANN (to American Cyanamid Co.). U. S. 1,819,792, Aug. 18. The reaction product of an org. dithiophosphate such as diamyl dithiophosphate and a basic compd. such as diphenylguanidine is used.

**Liquid heat-transfer medium suitable for use in vulcanizing apparatus.** THOMAS A. MOORMANN (to Shaler Co.). U. S. 1,820,085, Aug. 25. The medium consists of glycerol 80-90, ethylene glycol 20-10 and water 1 part.

**Treating rubber to retard deterioration.** WM. P. TER HORST (to Naugatuck Chemical Co.). U. S. 1,822,548, Sept. 8. A reaction product of a ketone such as acetone and a salt of an aromatic amino compd. such as *o*-toluidine-HCl (suitably in the proportion of about 1%) is added to rubber. Numerous other similar compds. also are mentioned as suitable. Cf. *C. A.* 25, 844.

**Use of rubber oil in preparing aqueous dispersions of organic substances such as rubber compounding ingredients.** ANDREW SZEGVARI (to American Anode, Inc.). U. S. 1,822,249, Sept. 8. Rubber oil is mixed with the material to be dispersed and the mixt. is then dispersed in water

**Electrodeposition of rubber and like materials.** FREDERICK H. LANE (to American Anode, Inc.). U. S. 1,822,226, Sept. 8. The optimum c. d. for the electrodeposition is detd. by electrodepositing the material from an aq. dispersion upon a surface over which the c. d. varies from one end to the other, and the c. d. is noted which effects the formation of a deposit of the desired characteristics. App. is described.

**Lining pipes with rubber by electrodeposition.** JAMES W. SCHADE (to American Anode, Inc.). U. S. 1,822,240, Sept. 8. An elec. current is passed through a liquid latex between the pipe and a cathode contained within a porous diaphragm within the pipe, while the cathode moves continuously along the axis of the pipe. App. is described.

**Recovery of constituents of waste rubber tires and like material.** JAMES W. AMES. U. S. 1,821,049, Sept. 1. A mass of material such as rubber and cement carried on old vehicle rims is burned to consume the combustible constituents and mineral substances are sepd. from the burning mass. App. is described suitable for the recovery of ingredients such as Zn compds. by this method.

**Preventing scorching of rubber in vulcanizing.** ERNEST R. BRIDGWATER (to E. I. du Pont de Nemours & Co.). U. S. 1,822,561, Sept. 8. A Cd compd. such as Cd oxide, hydroxide, stearate or oleate is added to a rubber mix contg. S and an accelerator of the substituted thiurammonosulfide type.

**Apparatus for vulcanizing tires.** LEO O. GRANGE (to Walter J. Jarratt). U. S. 1,822,590, Sept. 8. Structural features of an electrically heated app. with thermostatic control.



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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT AT THE OHIO STATE UNIVERSITY]

## NATURAL AND SYNTHETIC RUBBER. VIII. PRODUCTS OF THE DESTRUCTIVE DISTILLATION OF SODIUM RUBBER

BY THOMAS MIDGLEY, JR., A. L. HENNE AND A. F. SHEPARD

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In the first paper<sup>1</sup> of this series it was shown that the pyrolysis products of natural rubber are directly related to the rubber molecule. The pyrolysis products of sodium rubber should bear a similar relationship to its molecular structure, and the difference between its formula and that of natural rubber should be detected by a study of these products.

Four kilograms of sodium rubber was destructively distilled. The resulting hydrocarbons were separated by fractional distillation, and identified by the methods previously employed.<sup>1</sup> The results are summarized in Table I. The starred compounds were identified by methods described in the experimental part. The components marked "abridged" were noted

TABLE I  
COMPOUNDS, IDENTIFICATIONS AND QUANTITIES

Compounds	Degree of identification	Percentage in distillate
Propylenes and butenes	Positive	0.3
$\text{CH}_3\text{CH}(\text{CH}_3)\text{CH}=\text{CH}_2$	Positive	0.2
$\text{CH}_2=\text{C}(\text{CH}_3)\text{CH}_2\text{CH}_3$	Positive	2.0
$\text{CH}_2=\text{C}(\text{CH}_3)\text{CH}=\text{CH}_2$	Positive	1.1
$\text{CH}_3\text{C}(\text{CH}_3)=\text{CHCH}_3$	Positive	4.2
Component boiling at 58°	Abridged	0.05
3-Methylpentenes	Positive	.4
Component boiling at 68°	Abridged	.1
*Benzene	Positive	.1
*Isomeric heptane	Positive	.03
Component boiling at 93-95°	Abridged	.1
Tetrahydrotoluene	Positive	.4
Toluene	Positive	.1
Component boiling at 121-122°	Abridged	.2
*Hexahydroxylene	Possibly present	.1
* <i>o</i> -Xylene	Uncertain	.006
* <i>m</i> -Xylene	Positive	.1
* <i>p</i> -Xylene	Positive	.02
Compounds with 9 carbon atoms	Similar to those from natural rubber but not investigated	.5
*Compounds with 10 carbon atoms	Similar to those from natural rubber but in too small an amount to separate properly	6.4
*Dipentene	Uncertain	0.1

Normal pentane, isopentane and dihexahydroxylene were absent.

<sup>1</sup> Midgley and Henne, *J. Am. Chem. Soc.*, **51**, 1215-1226 (1929).

during the course of the fractionation, but were not investigated more fully due to the limited amount of available material.

The sodium rubber used was benzene-free. Hence the presence of benzene among the distillation products confirms the viewpoint of its origin as expressed in paper I.

*m*-Xylene is not the only xylene formed. This agrees with the expectations based on the structure of sodium rubber indicated in a previous paper.<sup>2</sup> Mass action considerations predict the ratio of ortho:meta:para-xylene as 5:10:5, but actually it is found to be <1:10:2. The reduction of the *o*-isomer can be explained by the assumption made in paper I that free valences on secondary or tertiary carbon atoms will accept hydrogen rather than form rings. This does not explain the decrease of the *p*-isomer. It may be assumed that during the polymerization of isoprene, a directive force causes the 1,4-type of linkage of isoprene units to be favored. The result is a molecule more nearly resembling the natural rubber molecule in methyl group spacing than would be expected.<sup>3</sup>

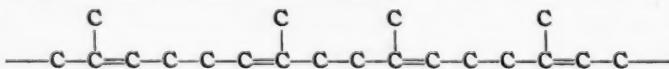
## Discussion

The comparison of the foregoing table with the similar table in paper I of this series is of primary interest. The significant similarities and differences in the pyrolysis products may be summarized as follows.

The arrangements of carbon atoms in the compounds obtained from natural and sodium rubber are the same, except for the position of some methyl groups. Compounds with five and ten carbon atoms predominate in both cases.

The products obtained from sodium rubber are more saturated. This is shown by the decrease of the quantities of isoprene and dipentene, the increase of the amount of pentenes, and the appearance of small amounts of saturated hydrocarbons. The last were entirely absent in the natural rubber distillate.

These results together with the postulates of paper I confirm the carbon arrangement in the sodium rubber formula



but disagree with the conception of a recurring double bond. Bromine titration indicates one double bond per  $C_6H_8$  unit. Ozonation gives an ozonide ( $C_6H_8O_3$ ), but this ozonide does not break down on heating with water to give the simple compounds expected.<sup>4</sup>

Overvulcanized rubber behaves, in many respects, like sodium rubber.

<sup>3</sup> Ref. 1, pp. 1294-1296.

<sup>8</sup> Steimmg, *Ber.*, 47, 350 (1914), has made a similar observation in his work on the ozonation of various synthetic rubbers.

<sup>4</sup> Harries, *Ann.*, 383, 217 (1911); 395, 241 (1913); 406, 180 (1914).

It still has one double bond for each sulfur-free  $C_6H_8$  unit, as shown by the fact that these will accept two atoms of bromine, or one molecule of ozone. The ozonide is not severed into simple molecules by treatment with water. Pyrolysis yields little isoprene or dipentene, but considerable amounts of pentenes and decomposition products which are substantially the same as those obtained from sodium rubber.

Hence it may be concluded that the structural formula of sodium rubber is a modification of the one given above involving hydrogen migration or cyclization of such a nature that one chemically weak bond results for each  $C_6H_8$  group and that this formula is a sulfur-free example of a rearrangement that occurs to some extent during the vulcanization of natural rubber.

### Experimental Part

The sodium rubber used in this work was prepared by polymerizing boiling isoprene with liquid sodium-potassium alloy. The isoprene was prepared by the careful fractionation of the pyrolysis products of crepe rubber; it boiled at 31-35°, contained no benzene, and titration indicated 1.8 double bonds. The unpolymerized material was removed from the rubber by distilling from a steam-bath. The distillate consisted chiefly of 2-methyl-1-butene and 2-methyl-2-butene together with about 25% of unpolymerized isoprene.

A 3.86-kg. batch of this rubber which still contained the sodium-potassium alloy<sup>6</sup> was then destructively distilled in the manner previously described.<sup>1</sup> A condenser cooled with carbon dioxide snow was used to catch the more volatile materials. This condensate was warmed to room temperature and the escaping vapor passed into a solution of bromine in carbon tetrachloride. Fractional distillation yielded only 35 g. of propylene and butene dibromides boiling at 140-162° and having  $d_4^{20}$  1.78.

The remainder of the hydrocarbons were separated and identified by the same methods as were previously employed, except as specifically mentioned hereafter. Due to the limited amount of material available, the complete identifications of certain minor constituents were omitted to make possible the investigation of other more important points. These cases are marked "abridged" in Table I.

**Benzene.**—The method of Rhodes, Gardner and Lewis<sup>6</sup> was first employed to investigate the presence of benzene in a cut boiling at 76-80°. In ethylene bromide this cut showed a mean molecular weight of 87. In benzene, molecular weights of 107.5, 110 and 107 were found. The presence of 17.5% of benzene is thus indicated. The remainder of the cut was then brominated and steam distilled. After treatment

<sup>6</sup> The presence of sodium-potassium alloy is not primarily responsible for the relatively low unsaturation of sodium rubber distillates. This is shown by the percentages of isoprene yielded in the fractions boiling from 32-38° on pyrolysis of 100 g. batches of the following

Crepe rubber.....	65% isoprene
Crepe rubber + 6% Na-K.....	55% isoprene
Sodium rubber, alloy free.....	35% isoprene
Sodium rubber + 1% Na-K.....	18% isoprene

<sup>6</sup> Rhodes, Gardner and Lewis, *Ind. Eng. Chem.*, 20, 85 (1928).

with sulfuric acid, nitration gave dinitrobenzene, which was purified and identified by a mixed melting point determination with authentic material.

The formol reaction of Linke<sup>7</sup> was used to establish the absence of any significant quantity of benzene in the isoprene from which the rubber was prepared. This reaction detects less than 0.1% of benzene in petroleum ether. A mixture of 25 cc. of isoprene and 2 cc. of pure *n*-heptane was saturated with bromine at 0° and the product steam distilled to bring over the heptane. The heptane was washed three times with concentrated sulfuric acid, and three drops of it were added to a mixture of 3 cc. of concentrated sulfuric acid and 2 drops of formaldehyde. No precipitate was formed. When the test was repeated with 0.02% benzene added to the isoprene, the characteristic precipitate was obtained in abundance.

**Xylenes.**—By bromination and steam distillation of several cuts boiling from 134–142°, a fraction rich in xylene was isolated. This fraction boiled at 136–142° and had  $d_4^{20}$  0.827,  $n_D^{20}$  1.4630 and a molecular weight in benzene of 112 and 112. The presence of a saturated hydrocarbon along with xylenes is thus indicated. A portion of this material was nitrated by the procedure of Mulliken<sup>8</sup> and the crude mixture of nitro compounds was subjected to crystallization from alcohol; 77% of the nitro compound was recovered as trinitro-*m*-xylene, which was identified by a mixed melting point with authentic material.

*Anal.* Calcd. for  $C_8H_7N_3O_6$ : N, 17.42. Found: N, 17.29, 17.36.

From the mother liquors were obtained by recrystallization 14% of trinitro-*p*-xylene identified by a mixed melting point with authentic material.

An attempt was made to determine quantitatively the amounts of *o*- and *p*-xylenes present by a method similar to that used for benzene. The method was not quantitatively satisfactory due to the abnormal behavior of *o*- and *p*-xylenes as cryoscopic solvents. The results, however, did agree qualitatively with those obtained by the nitration method.

The oxidation of a small amount of the crude xylenes with potassium permanganate produced an acid which gave the fluorescein test for phthalic acid. This is evidence of the presence of *o*-xylene in small amount, estimated to be less than 0.006% of the original rubber.

**Compounds with Ten Carbon Atoms.**—More than 6% of the total distillate consisted of compounds boiling from 158–176°. Prolonged fractionation failed to separate the components satisfactorily; fractionation from aniline was likewise of little value. Molecular weight determinations in benzene for the fractions in this range gave values from 133–139°. The two largest cuts in this range were examined more closely after aniline fractionation. The cuts boiled at 160–162.5° and 173–5.5° on Engler distillation and each comprised about 30% of the material boiling from 158–176°. The experimental data concerning these components are summarized below.

**Component 160–162.5°:**  $d_4^{20}$  0.826;  $n_D^{20}$  1.4627; mol. wt. in benzene 133, 133; double bonds 1.15. Combustion showed C, 87.44, 87.58; H, 12.14, 12.19, which is an empirical composition of  $C_{10}H_{16.6}$ . On hydrogenation 1.2 moles of hydrogen were absorbed. The resulting material boiled at 162–164°, and had  $d_4^{20}$  0.791,  $n_D^{20}$  1.4369, and mol. wt. in benzene 138, 139.

**Component 173–175.5°:**  $d_4^{20}$  0.837;  $n_D^{20}$  1.4709; mol. wt. in benzene 137, 136; double bonds 1.6. Combustion gave C, 87.61, 87.79; H, 12.15, 12.03, which is an empirical formula of  $C_{10}H_{16.4}$ . On hydrogenation 1.7 moles of hydrogen were absorbed;

<sup>7</sup> Linke, *Ber.*, 11, 258–262 (1901); *Chem. Zentr.*, II, 130 (1920).

<sup>8</sup> S. P. Mulliken, *Identification of Pure Organic Compounds*, John Wiley and Sons, New York, 1904, Vol. I, p. 202.

the product boiled at 170.5-172.5° and had  $d_4^{20}$  0.804,  $n_D^{20}$  1.4425 and mol. wt. in benzene of 139, 139. No dipentene tetrabromide could be obtained when the original hydrocarbon was brominated.

**Saturated Compounds.**—Various cuts were examined for saturated compounds by brominating, steam distilling, washing with sulfuric acid, redistilling and finally nitrating with mixed acid, washing with sulfuric acid and again redistilling. The observations are tabulated.

Boiling range, °C.	$d_4^{20}$	$n_D^{20}$	Mol. wt.	Percentage in total distillate	Remarks
ca. 75				0.003	Presence evident from low density and refractive index of benzene specimen.
92-93	0.726	1.4023		.03	Paraffin hydrocarbon present.
119-122	.765	1.4203	112, 112.5	.1	Naphthenic hydrocarbon present, presumably hexahydroxylene.
136-142	.78*		118*	.1	Presumably a naphthenic hydrocarbon.

\* The properties of this material were extrapolated from those of the xylene fraction after determination of the amount of saturated hydrocarbon by the procedure of Spielman and Jones.<sup>9</sup>

**Ozonation of Sodium Rubber and of Overcured Rubber.**—The sodium rubber was purified before ozonation by the following procedure. A sample was dissolved in benzene, and alcohol was slowly added to react with the sodium-potassium alloy and to precipitate the rubber. The rubber was boiled out with water and then redissolved in benzene and reprecipitated with alcohol twice more. After removal of solvents in vacuum, a double bond determination by the method of Lewis and McAdams<sup>10</sup> showed the presence of 1.0 double bond per  $C_6H_6$  unit.

TABLE II

## ANALYSES OF OZONIDES

	C, %	H, %	S, %	Empirical formula			
Sodium rubber ozonide	54.65	55.05	7.29	$C_6H_6O_{2.6}$			
Water-insoluble material from sodium rubber ozonide	65.37	65.47	7.55	$C_6H_6.8O_{1.65}$			
Overcured rubber ozonide	53.39	53.30	6.44	$[(C_6H_6S)(C_6H_6O_3)_{6.14}]_n$			
First water extract from overcured rubber ozonide	49.2	6.6	1.86	1.97	.....		
Second water extract from overcured rubber ozonide	52.64	52.55	6.23	6.43	4.66	4.80	.....
Solid insoluble in water from overcured rubber ozonide	61.21	61.28	6.16	6.18	5.32	5.38	.....

<sup>9</sup> Spielman and Jones, *J. Soc. Chem. Ind.*, **36**, 489-490 (1917).

<sup>10</sup> Lewis and McAdams, *Ind. Eng. Chem.*, **12**, 673 (1920).

The overcured rubber was prepared by curing a rubber-sulfur mix for 150 hours at 150°. Analysis showed 5.7% combined sulfur and 0.11% free sulfur; a double bond determination indicated 0.84 double bond per  $C_6H_6$  unit.

Ozonation of the samples was carried out in carbon tetrachloride to which 5% of glacial acetic acid was added. Solvent loss was made up by adding more acetic acid. The sodium rubber was soluble in this mixture, while it was necessary to grind the overcured rubber finely and suspend it in the solution. Solvents were removed from the ozonides in high vacuum. On boiling the ozonides with water only traces of material of low molecular weight were obtained. In each case about half the ozonide was dissolved by the water and could be thus separated; the remainder formed a solid. Analyses of the ozonides and of various fractions separated by water are given in Table II. The sample of sodium rubber ozonide had turned very black during the removal of solvents in vacuum.

### Summary

The pyrolysis products of sodium rubber have been compared with those of natural rubber. They indicate that sodium rubber is isomeric with natural rubber in the positioning of its methyl groups, and that the double bond of sodium rubber differs from the true ethylenic bond of natural rubber. In the latter respect sodium rubber closely resembles overvulcanized rubber.

COLUMBUS, OHIO

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## ACETYLENE POLYMERS AND THEIR DERIVATIVES. II. A NEW SYNTHETIC RUBBER: CHLOROPRENE AND ITS POLYMERS

BY WALLACE H. CAROTHERS, IRA WILLIAMS, ARNOLD M. COLLINS AND JAMES E. KIRBY

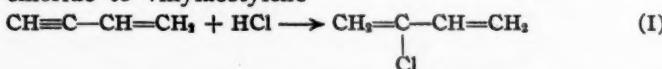
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Study of the reactions of vinylacetylene, a compound which has become available through discoveries described in the preceding paper,<sup>1</sup> has led to the synthesis of a series of new analogs and homologs of isoprene. The present paper is concerned with one of the simplest of these, namely, chloro-2-butadiene-1,3 (I). This compound is especially interesting for the following reasons. It is easily prepared in quantity in a state of purity; it differs structurally from isoprene only in having a chlorine atom instead of a methyl group; like isoprene it reacts with itself to yield a synthetic rubber; but the transformation occurs with much greater velocity than in the case of isoprene; and the product is distinctly superior to natural rubber in some of its properties.

In order to recognize the analogy in structure and behavior which exists between isoprene and chloro-2-butadiene-1,3, we call the latter compound *chloroprene*, and this name also serves to distinguish it from other chlorobutadienes that will be described in future papers.

**Preparation of Chloroprene.**—Chloroprene is obtained by the addition of hydrogen chloride to vinylacetylene



Other products, which will be described in future papers, are also formed by the action of hydrogen chloride on vinylacetylene under certain conditions; but under the conditions indicated in the following example, chloroprene is practically the only product.

Fifty grams of cold vinylacetylene is placed in a pressure bottle containing a thoroughly chilled mixture composed of 175 g. of concd. hydrochloric acid (sp. gr. 1.19), 25 g. of cuprous chloride, and 10 g. of ammonium chloride. The bottle is placed in a water-bath, the temperature of which is held at approximately 30°, where it is shaken for a period of four hours. The contents of the bottle are placed in a separatory funnel, the lower aqueous layer is drawn off, and the oily layer is washed with water, dried with calcium chloride, mixed with a small amount of catechol or pyrogallol and distilled *in vacuo* through an efficient column provided with a refrigerated dephlegmator and receiver. Pure chloroprene is thus obtained in yields of about 65% of the theo-

<sup>1</sup> Nieuwland, Calcott, Downing and Carter, *J. Am. Chem. Soc.*, 53, 4197 (1931).

retical based on the vinylacetylene applied. Some vinylacetylene is recovered in the distillation. The yields can be considerably improved if the chloroprene is separated from the reaction mixture by steam distillation *in vacuo* (100–250 mm.).

**Physical Properties and Analysis.**—Chloroprene is a colorless liquid with a characteristic ethereal odor, somewhat resembling ethyl bromide. It is miscible with most of the common organic solvents, but only slightly soluble in water. Some of its other properties are boiling point,<sup>2</sup> 59.4° at 760 mm., 46.9° at 500 mm., 40.5° at 400 mm., 32.8° at 300 mm., 6.4° at 100 mm.; vapor pressure,  $\log_{10} v. p. (\text{mm. Hg}) = -1545.3/T(\text{abs}) + 7.527$ ; calculated molal latent heat of evaporation, 7,090 cal.; density,  $d_{20}^{20}$  0.9583; refractive index,  $n_c^{20}$  1.4540,  $n_D^{20}$  1.4583,  $n_F^{20}$  1.4690.

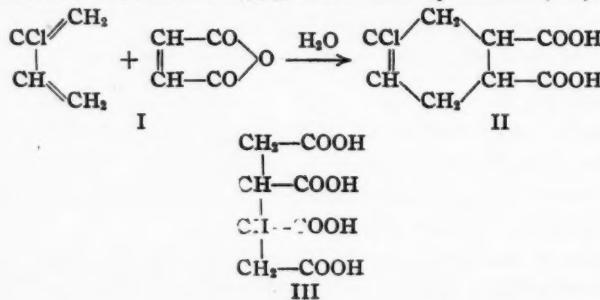
Found	$M_c$ 25.06	$M_D$ 25.26
Calcd.	24.67	24.66
Difference	0.39	0.60

Viscosity at 25°, 0.394 centipoise.

*Anal.* Calcd. for  $C_4H_5Cl$ : C, 54.25; H, 5.69; Cl, 40.06; mol. wt., 88.5. Found: C, 54.37; H, 5.95; Cl, 39.51, 38.81; mol. wt. (in freezing benzene), 89.0, 89.0.

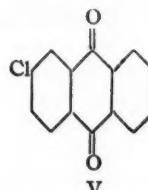
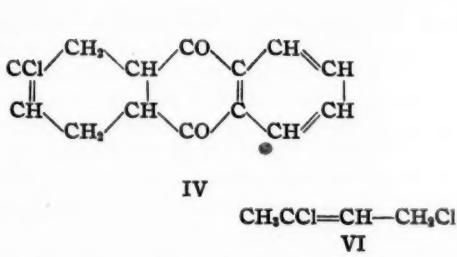
**Chemical Properties and Proof of Structure.**—The structure of chloroprene as chloro-2-butadiene-1,3 is established by its analytical composition and by the following reactions.

It reacts readily with maleic anhydride and yields, after hydrolysis with water, a crystalline product to which we assign the structure chloro-4-tetrahydro-1,2,3,6-phthalic acid (II). The chlorine atom of this product, in accordance with its assumed structure, is very resistant to the action of concentrated boiling alkali, and oxidation with boiling nitric acid yields a crystalline compound identical in melting point and composition with the known acid, butane- $\alpha, \beta, \gamma, \delta$ -tetracarboxylic acid (III).



Chloroprene further reacts readily with naphthoquinone, and the primary product, which presumably has the structure chloro-2-tetrahydro-1,4,4a,9a-anthraquinone-9,10 (IV), is smoothly oxidized by air in the presence of alkali to  $\beta$ -chloroanthraquinone (V). The identity of this is established by the method of mixed melting point.

<sup>2</sup> These data are based on vapor pressure measurements made with an isoteniscope by H. W. Starkweather.



In view of the recent studies of Diels and Alder<sup>3</sup> this result decisively demonstrates the presence in chloroprene of a pair of conjugated double bonds, and it fixes unequivocally the position of the chlorine atom.

In chloroform solution chloroprene readily adds approximately two atoms of bromine before substitution begins. It rapidly decolorizes alkaline permanganate solution. In the presence of cuprous chloride it reacts with aqueous hydrochloric acid. The reaction consists in 1,4-addition and the product is dichloro-1,3-butene-2 (VI), which will be described in a future paper. The chlorine atom of chloroprene is very firmly bound. Only traces of chloride ion appear on boiling with alcoholic silver nitrate, alcoholic sodium hydroxide, or pyridine.

**Reaction of Chloroprene with Maleic Anhydride. Preparation of Chloro-4-tetrahydro-1,2,3,6-phthalic Acid (II).**—21.2 g. of chloroprene was warmed with 19.6 g. of maleic anhydride. The anhydride dissolved readily and when 50° was reached sufficient heat was developed from the reaction to maintain this temperature for some time. After standing overnight the reaction product was boiled with 200 cc. of water to remove unchanged chloroprene and filtered. On cooling stout rectangular plates separated; yield 31.5 g. or 77% of the theoretical; m. p. 171–172° (corr.). Recrystallization from water raised the melting point to 173–175°.

*Anal.* Calcd. for  $C_8H_8O_4Cl$ : C, 46.94; H, 4.43; Cl, 17.34; neutral equivalent, 102.3. Found: C, 47.54; H, 4.78; Cl, 17.24, 17.71; neutral equivalent, 103.5.

The acid was boiled with 25% potassium hydroxide for three hours. No significant quantity of chloride ion was produced. This indicates that the chlorine is attached to a double-bonded carbon atom.

**Oxidation to Butane- $\alpha, \beta, \gamma, \delta$ -tetracarboxylic Acid (III).**—A sample (8.2 g.) of the above-described acid was warmed with 30 g. of 70% nitric acid until a rather violent reaction took place with the evolution of nitrogen oxides. The unused nitric acid was removed *in vacuo* and the partly crystalline residue taken up in a small volume of hot water. On cooling a thick mass of flat needles with square ends separated. After a second crystallization, the product melted at 192–193° with effervescence.

*Anal.* Calcd. for  $C_8H_{10}O_8$ : C, 41.05; H, 4.27; neutral equivalent, 58.5. Found: C, 41.32, 41.46; H, 4.66, 4.67; neutral equivalent, 58.8.

This acid has already been described by Auwers and Jacob<sup>4</sup> and also by Farmer and Warren.<sup>5</sup>

<sup>3</sup> Diels and Alder, *Ber.*, **62**, 2337 (1929).

<sup>4</sup> Auwers and Jacob, *ibid.*, **27**, 1114 (1894).

<sup>5</sup> Farmer and Warren, *J. Chem. Soc.*, 897 (1929).

**Action of  $\alpha$ -Naphthoquinone on Chloroprene.** Conversion to  $\beta$ -Chloroanthraquinone.—To 10 g. of naphthoquinone dissolved in benzene 12 g. of chloroprene was added. The mixture was refluxed for three hours and then allowed to stand overnight. The benzene was removed under reduced pressure, and the residual mass was dissolved in warm alcohol and cooled. A considerable amount of unchanged naphthoquinone separated. This was filtered off. Dilution of the mother liquor with water gave a solid which separated from alcohol in fine needles melting at 76°. It was still contaminated with naphthoquinone. It was suspended in alcohol containing a little sodium hydroxide, and air was bubbled through the suspension for twenty minutes. The suspended solid was crystallized three times from amyl alcohol; small needles, m. p. 209.5°; mixed melting point with  $\beta$ -chloroanthraquinone, 209.5°.

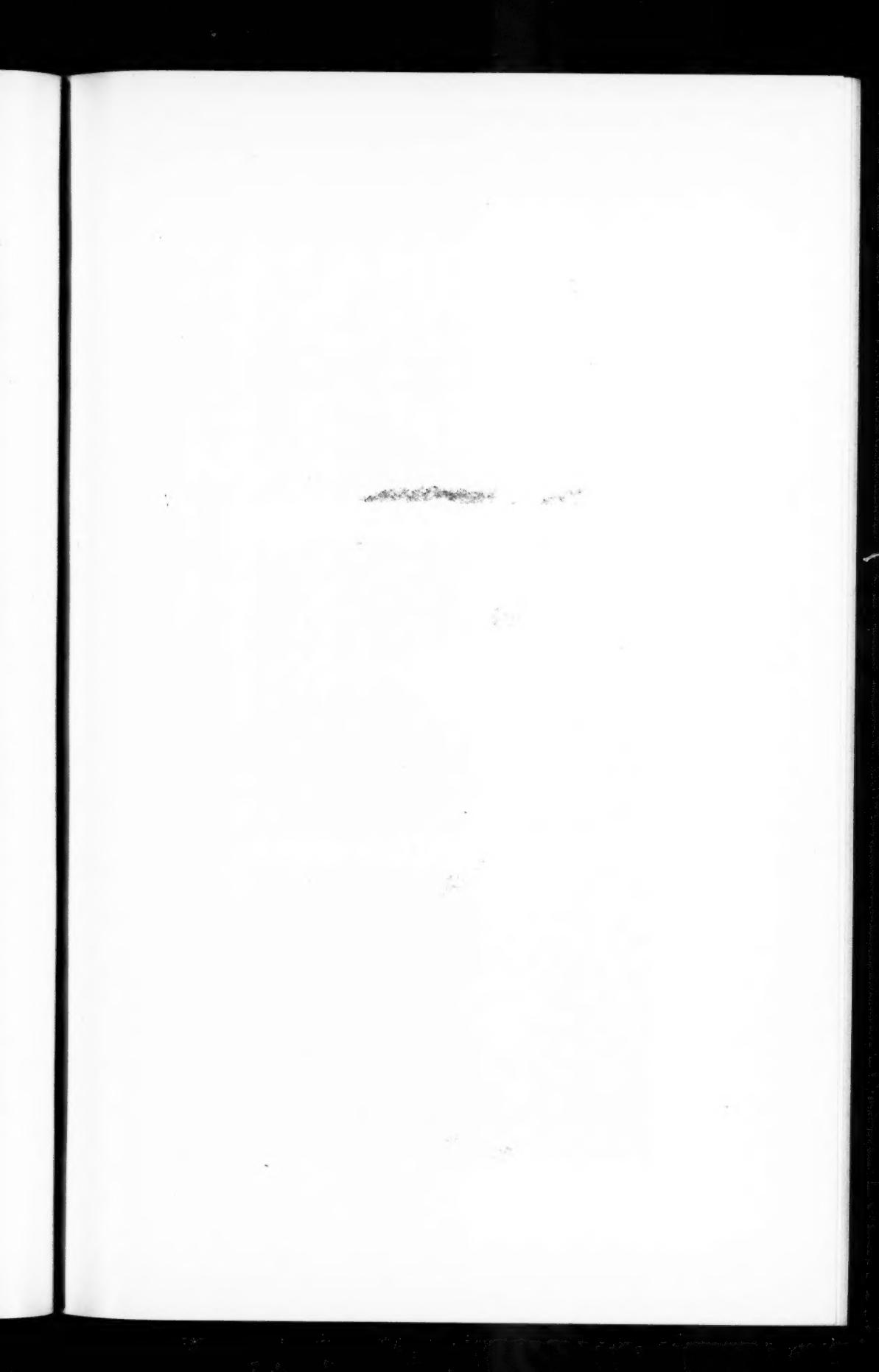
**Spontaneous Polymerization of Chloroprene.**—The following example is typical of the spontaneous polymerization of chloroprene.

About 40 cc. of chloroprene is placed in a 50-cc. bottle of soda glass, closed with a cork stopper, and allowed to stand at the laboratory temperature (about 25°) in the absence of direct light. After twenty-four hours the viscosity of the sample has considerably increased; after four days it has set to a stiff, colorless, transparent jelly, which still contains a considerable amount of unchanged chloroprene. As the polymerization proceeds further this jelly contracts in volume and becomes more tough and dense. After ten days all the chloroprene has polymerized. We call this product  $\mu$ -polychloroprene to distinguish it from other chloroprene polymers that will be described later in this paper.

**Properties of  $\mu$ -Polychloroprene.**—The product of the above-described reaction is a colorless or pale yellow, transparent, resilient, elastic mass resembling a completely vulcanized soft rubber. Its density at 20° is about 1.23, and its refractive index ( $n_D^{20}$ ) is about 1.5512. It has a tensile strength of about 140 kg. per sq. cm. and an elongation at break of about 800%. It is not plastic; that is, it does not sheet out smoothly on the rolls of the rubber mill nor break down on continued milling. It is not thermoplastic. It swells strongly but does not dissolve in carbon tetrachloride, carbon disulfide, benzene, nitrobenzene, pyridine, aniline, ethyl acetate and ether. Compared with natural rubber the tendency of this material to imbibe gasoline and lubricating oil is very slight. When a stretched sample is immersed in liquid air for a moment and then struck with a hammer it shatters into fibrous fragments.<sup>6</sup>

The properties of the  $\mu$ -polymer vary somewhat depending upon the conditions under which it is formed. When the chloroprene has access to large amounts of air or oxygen during the polymerization the product is dark in color and harder and stiffer than otherwise. The polymer formed at elevated temperature is inclined to be soft and it has a distinct terpene-like odor. This is due to the presence of the volatile  $\beta$ -polymer, which will be described in a subsequent paragraph.

<sup>6</sup> The same behavior has already been observed in rubber by Hock, *Gummi-Ztg.*, 39, 1740 (1925).



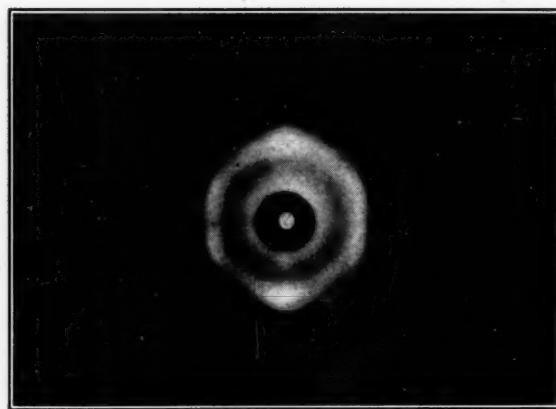


Fig. 1.—x-Ray diffraction pattern of  $\mu$ -polychloroprene (from latex) stretched 500%.

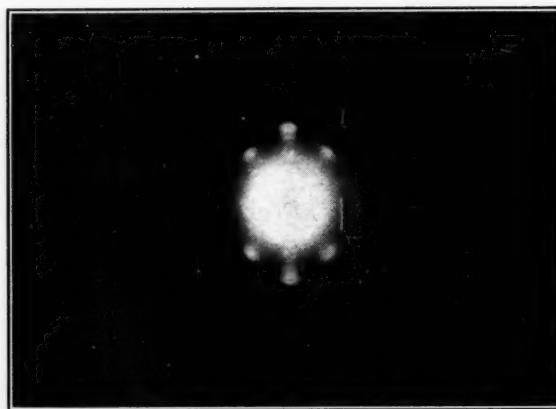


Fig. 2.—x-Ray diffraction pattern of  $\mu$ -cured smoked sheet rubber stretched 500%.

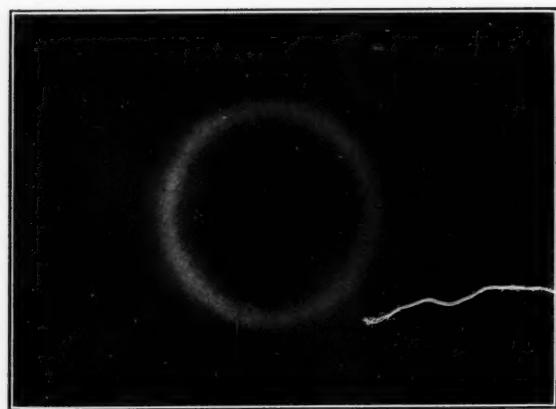


Fig. 3.—x-Ray diffraction pattern of  $\alpha$ -polychloroprene (unstretched).

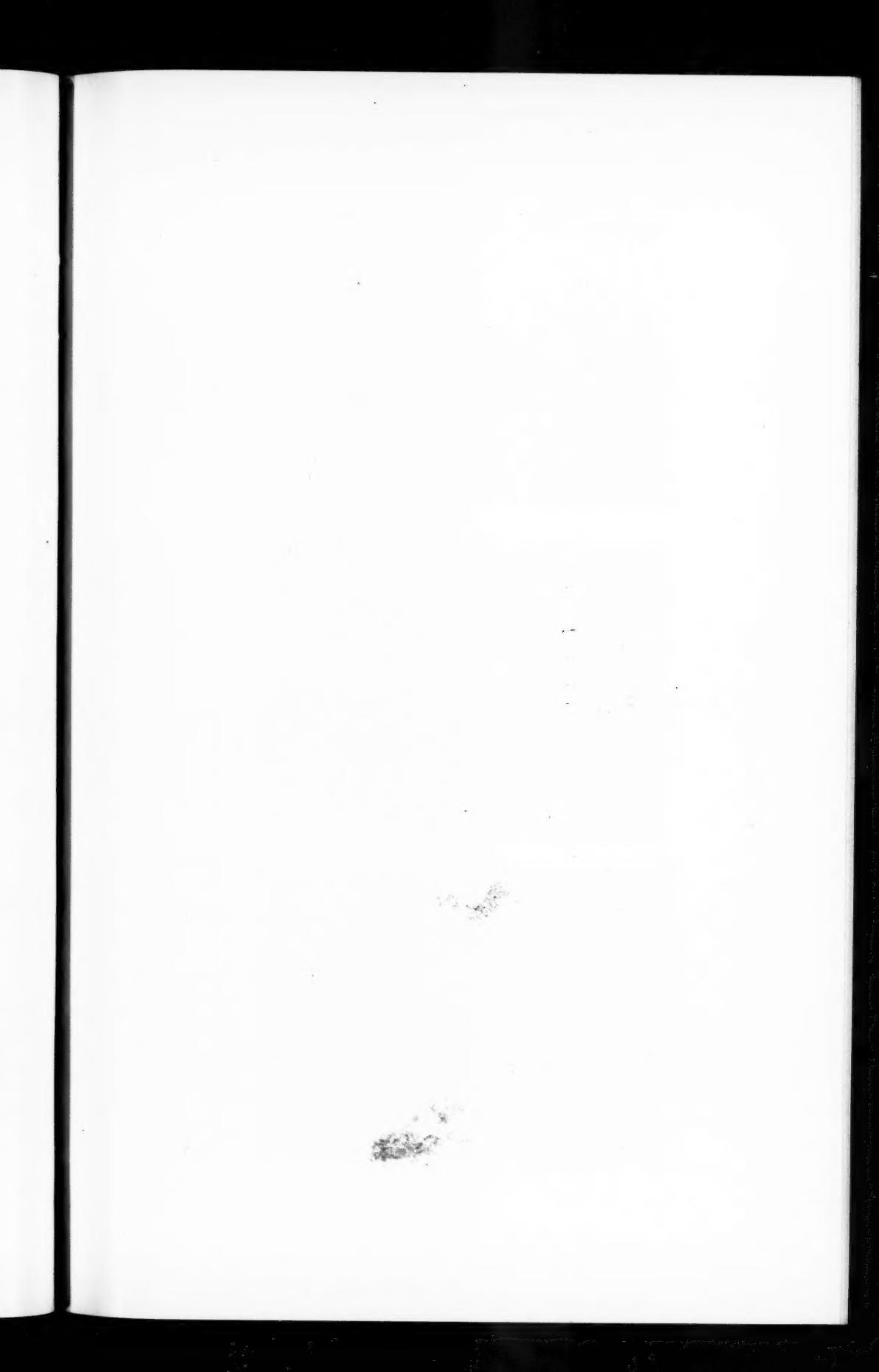




Fig. 3.—x-Ray diffraction pattern of  $\alpha$ -polychloroprene (unstretched).

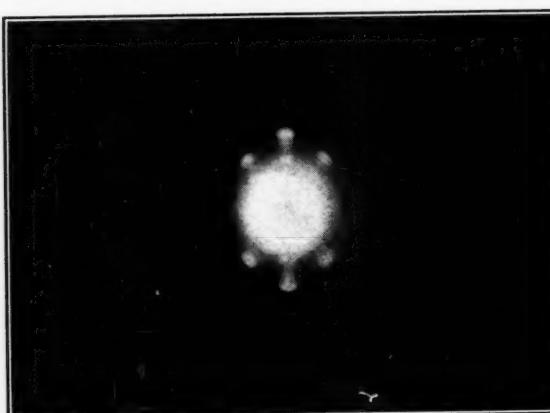


Fig. 2.—x-Ray diffraction pattern of  $\mu$ -lightly cured smoked sheet rubber stretched 500%.

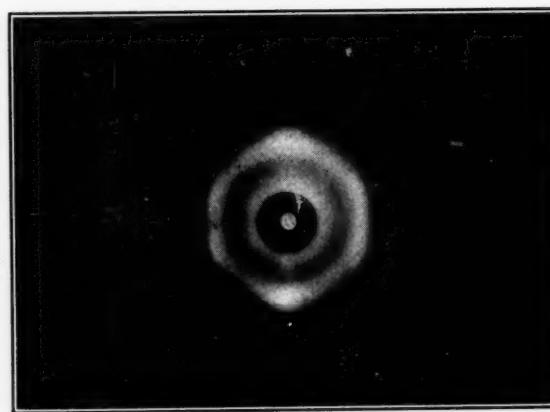


Fig. 1.—x-Ray diffraction pattern of  $\mu$ -polychloroprene (from latex) stretched 500%.

**x-Ray Diffraction Pattern.**—Although the x-ray diffraction pattern of unstretched rubber shows only a single diffuse ring, characteristic of a liquid or an amorphous solid, stretched rubber shows a point diagram.<sup>7</sup> On the other hand, according to Mark,<sup>8</sup> all synthetic, polymerized products from isoprene or other unsaturated hydrocarbons so far investigated have given, even when stretched, a diffraction pattern analogous to that of a liquid.

It is therefore a matter of considerable interest that the  $\mu$ -polychloroprene described above (as well as the cured plastic polymer described in a later paragraph), when stretched about 500%, exhibits a fully developed fiber diagram showing a number of definite layer lines. One of these diffraction patterns is reproduced in Fig. 1, together with a diagram of stretched rubber (Fig. 2). The identity period along the fiber axis is 4.8 Å. This length corresponds rather closely with the calculated length for one chloroprene unit. The agreement is better if one assumes a *trans* instead of a *cis* configuration since the calculated identity period in a *cis* polyprene chain is about  $2 \times 4.1$  Å., whereas in a *trans* chain it is about 4.8 Å.<sup>9</sup> Incidentally, 4.8 Å. is exactly the identity period observed for  $\beta$ -gutta-percha by Hauser and v. Susich.<sup>10</sup> Unstretched samples of polychloroprene give an amorphous ring (Fig. 3) entirely like natural rubber. The spacing corresponding to this ring is 4.86 Å. We are indebted to A. W. Kenney for these observations.

**Chemical Properties of  $\mu$ -Polychloroprene.**—The  $\mu$ -product has the composition required for an addition polymer of chloroprene.

*Anal.* Calcd. for  $(C_4H_6Cl)_n$ : C, 54.25; H, 5.69; Cl, 40.06. Found: C, 53.74, 54.83; H, 5.70, 5.93; Cl, 40.06, 39.32.

Molecular weight determinations are not possible on account of its lack of solubility.

The  $\mu$ -polymer is unsaturated toward bromine but no quantitative data on this point are yet available. The chlorine atoms are very firmly bound. Only slight traces of chloride ion are liberated when the compound is heated for six hours in boiling alcoholic potash or boiling pyridine. This fact suggests that the chlorine atoms of the polymer are still attached to carbon atoms bearing double bonds.

The oxidation of the  $\mu$ -polymer with hot nitric acid leads to the isolation of succinic acid.

No attempts have yet been made to degrade the  $\mu$ -polymer with ozone.

<sup>7</sup> Katz, *Chem.-Zig.*, 49, 353 (1925); Meyer and Mark, *Ber.*, 61, 1939 (1928).

<sup>8</sup> *Die Röntgentechnik in der Materialprüfung*, Eggert and Schiebold, Akademische Verlagsgesellschaft, Leipzig, 1930, p. 142.

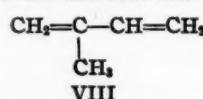
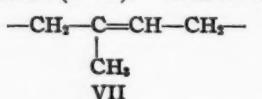
<sup>9</sup> Meyer and Mark, *Der Aufbau der hochpolymeren organischen Naturstoffe*, Akademische Verlagsgesellschaft, Leipzig, 1930.

<sup>10</sup> Hauser and v. Susich, *Kautschuk*, 7, 145 (1931).

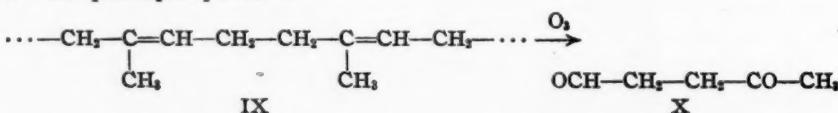
completely, but when stretched it is much more resistant than natural rubber to the deteriorating effect of ozone-containing air.

It is well known that purified rubber hydrocarbon is very susceptible to autoxidation. A similar and perhaps more exaggerated sensitivity is characteristic of synthetic rubbers derived from diene hydrocarbons. In this respect  $\mu$ -polychloroprene appears to be considerably more resistant. Nevertheless it does not long remain completely unaltered when freely exposed to air and light. It gradually becomes darker in color and finally after two or three weeks is dark brown. At the same time, it becomes harder, especially on the surface. These changes are accompanied by the liberation of traces of hydrogen chloride. The autoxidation can be suppressed by treating the polymer with small amounts of antioxidants.

**Chemical Structure of  $\mu$ -Polychloroprene.**—The molecules of natural rubber are long chains built up from the unit (VII) derived (formally) from isoprene (VIII). This structure follows from the fact that the ozoni-

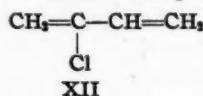
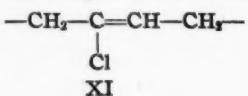


zation of rubber (IX) leads to levulinic acid and levulinic aldehyde (X) as the principal products.<sup>11</sup>

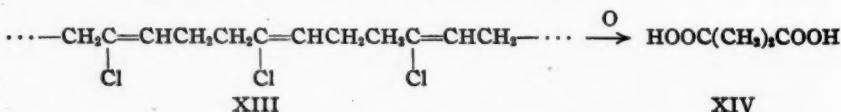


In their behavior toward ozone the so-called *normal* synthetic rubbers from isoprene very closely resemble the natural products,<sup>12</sup> and their molecules must therefore for the most part be built up on the same general plan.

Analogy suggests that the molecules of the chloroprene polymer are similarly built up from the units (XI) derived from chloroprene (XII).



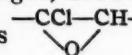
The resulting chains would have the formula XIII.



This formula readily accounts for the fact that oxidation of the  $\mu$ -polychloroprene yields succinic acid (XIV). It also explains why the chlorine

<sup>11</sup> Harries, *Ber.*, 37, 2708 (1904); 38, 3985 (1905); Pummerer, Ebermayer and Gerlach, *ibid.*, 64, 809 (1931).

<sup>12</sup> Harries, *Untersuchungen*, Julius Springer, 1919, p. 222.

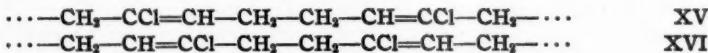
atom is very resistant to the action of alkalies: as in vinyl chloride, the chlorine is attached to a carbon atom bearing a double bond. This situation is changed, however, by autoxidation. This must lead to some such grouping as  , in which the chlorine atom would be exceedingly mobile.

Some evidence for this formula is also found in the physical properties of the  $\mu$ -polychloroprene. The molecular refractivity calculated for this formula (22.95) agrees exactly with the experimental value (22.95). The x-ray diffraction pattern indicates an identity period of 4.8 Å., which corresponds quite well with that calculated for one chloroprene unit.

It appears to be generally true that the presence of a chlorine atom at a double bond decreases the tendency of the double bond to react with ozone, and in this connection it is significant that  $\mu$ -polychloroprene is much more resistant than natural rubber to the deteriorating action of ozone.

In the formulas IX and XIII the isoprene and chloroprene units have been represented as being united regularly in 1,4-1,4- . . . order. The units, however, are not symmetrical and in joining of two units one or both of them might be inverted. This would lead to the arrangements 1,4-4,1- . . . and 4,1-1,4- . . . . It has been demonstrated that such inversions<sup>13</sup> do occur in the polymerization of isoprene in the presence of sodium and alcohol. On the other hand, isoprene rubber formed by thermal polymerization, since its behavior toward ozone is normal,<sup>14</sup> must be free from any considerable proportion of such inversions in its molecules.

The oxidation of  $\mu$ -polychloroprene to succinic acid gives no indication as to whether the arrangement of the units is normal as represented in XIII or inverted as in XV and XVI, since the latter would also yield succinic acid.



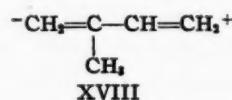
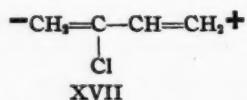
On the other hand, the fact that  $\mu$ -polychloroprene like natural rubber yields a sharp x-ray diffraction pattern whereas this property is absent from other synthetic rubbers perhaps indicates that the polychloroprene is freer from irregularities in the structure of its molecules than other synthetic rubbers.

The spontaneous polymerization of isoprene requires several years for its completion; with chloroprene the transformation is complete in a few days. The great difference in speed may be ascribed, in part at least, to the activating influence of the chlorine atom. The methyl group is too

<sup>13</sup> Midgley and Henne, *J. Am. Chem. Soc.*, **52**, 2077 (1930).

<sup>14</sup> Cf. Pummerer and Koch, in Memmler's *Handbuch der Kautschukwissenschaft*, S. Hirzel, Leipzig, 1930, p. 270.

feebly polar to exert any such effect. A similar difference exists between vinyl chloride and propylene in their tendency to polymerize. The chlorine atom here functions not only to activate powerfully the double bond, it also exerts a greater effect than methyl on the direction of addition reactions at the double bond: it more effectively controls the polarity of the molecule. A similar directive effect in chloroprene is demonstrated by its behavior toward hydrogen chloride. Thus the relation between chloroprene and isoprene may be symbolized by the formulas XVII and XVIII.



It seems highly probable therefore on theoretical grounds not only that the polymerization of chloroprene will proceed much more rapidly than the polymerization of isoprene, but that there will be much less chance of inversions of the units in the polychloroprene chains.

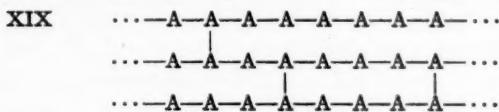
Formula XIII adequately represents the chemical behavior of  $\mu$ -polychloroprene, but it is not sufficiently complete to account for the remarkable physical behavior of this material. The difficulties in this connection are precisely the same as those presented by natural rubber. The linear polymeric structure partially represented in formula IX furnishes a sufficient basis for describing the chemical behavior of rubber. It is known further that the molecular weight of rubber is exceedingly high—perhaps in the neighborhood of 70,000;<sup>15</sup> but no entirely adequate explanation of the elastic properties of rubber in terms of this structure has been offered. It seems scarcely necessary to review the numerous speculations that have been devoted to this subject.<sup>16</sup> We merely point out that the units in a substituted polyprene chain (e. g., rubber or polychloroprene) present the possibility of geometrical isomerism and that they may be arranged in *cis-cis-cis*- · · · order or *trans-trans-trans*- · · · order; or both arrangements may be present in a single chain. The molecules may be coiled into spirals rather than rigidly extended. On these questions we have no data concerning polychloroprene (see, however, the above paragraph entitled x-Ray Diffraction Pattern). Moreover, we have no direct information concerning the molecular weight of polychloroprene. It seems certain, however, that the chains must be very long.

We observe finally that  $\mu$ -polychloroprene resembles vulcanized rather than unvulcanized rubber. It is not plastic; it does not become plastic when heated; and it does not dissolve but merely swells in rubber solvents

<sup>15</sup> Staudinger and Bondy, *Ann.*, **488**, 127 (1931).

<sup>16</sup> Some of the most suggestive are Staudinger, *Kautschuk*, **5**, 911, 1261 (1929); Meyer and Mark, *Der Aufbau der hochpolymeren organischen Naturstoffe*, Akademische Verlagsgesellschaft, Leipzig, 1930; Fikentscher and Mark, *Kautschuk*, **6**, 2 (1930).

such as benzene and chloroform. This behavior is much more consistent with a three-dimensional polymeric structure than with a simple linear structure. We assume therefore that in  $\mu$ -polychloroprene chains of the type already described are chemically linked together at occasional points. The resulting structure as we conceive it may be symbolized by formula XIX in which A stands for the structural unit. The cross-linking may occur through the mediacy of oxygen atoms, but it seems more likely that the double bonds of parallel chains mutually saturate one another directly. Since the chains are exceedingly long they need to be linked together only at occasional points to produce a non-plastic structure.



**$\beta$ -Polychloroprene.**—When chloroprene is polymerized at elevated temperature, *e. g.*, at 60° especially in the absence of air, the product is somewhat less dense and softer than that formed at ordinary temperature, and it has a pronounced terpene-like odor. This odor is due to the presence of volatile chloroprene polymers ( $\beta$ -polymer). This product can be prepared in quantity by storing or heating chloroprene in the presence of substances such as pyrogallol or trinitrobenzene that inhibit the transformation of chloroprene into the  $\mu$ -polymer. By distillation the  $\beta$ -polymer can be separated into two fractions, one boiling at 92 to 97° at 27 mm. and the other boiling chiefly at 114 to 118° at 27 mm. The odor of the fractions is very similar—fragrant and terpene-like. The constitution of these products has not been determined, but there is little doubt that they are cyclic dimers of chloroprene. It is already known that analogous products are formed from isoprene,<sup>17</sup> butadiene<sup>18</sup> and dimethylbutadiene.<sup>19</sup> The  $\beta$ -polychloroprenes are stable substances, which show no tendency to polymerize further. They have therefore no direct bearing on the formation of the rubber-like polymers, and they are relatively unimportant, especially since they appear in significant amounts only under rather exceptional conditions.

**Influences Affecting the Polymerization of Chloroprene.**—A few typical data are assembled in Table I.

(a) **Catalysts.**—Oxygen is an exceedingly powerful catalyst for the transformation of chloroprene into the  $\mu$ -polymer. Samples of chloroprene distilled in high vacuum and sealed off in glass tubes without exposure to the air show an appreciable increase in viscosity only after a period of one or two months, and the transformation to  $\mu$ -polymer is still

<sup>17</sup> Pummerer and Koch, *loc. cit.*, p. 284.

<sup>18</sup> Hofmann and Tank, *Z. angew. Chem.*, **25**, 1465 (1912).

<sup>19</sup> Van Romburgh and Van Romburgh, *Proc. Roy. Acad. Amsterdam*, **34**, 224 (1931).

TABLE I

ESTIMATED TIME REQUIRED FOR 90% OF A SAMPLE OF CHLOROPRENE TO POLYMERIZE  
UNDER VARIOUS CONDITIONS (ABSENCE OF DIRECT LIGHT)

No.	Temp., °C.	Air	Conditions		Time, days	Character of product
			Pressure, atm.	Other added substances		
1	25	Present	1	None	8	Colorless, strong, tough
2	25	Absent	1	None	400	Soft, low density, strong odor of dimer
3	62	Present	1	None	2	Strong, tough, slight odor of dimer
4	62	Absent	1	None	10	Strong, tough, odor of dimer
5	100	Absent	1	None	< 1	Semi-fluid, black, much dimer
6	25	Present	4500	None	< 2	Transparent, rather hard, very tough
7	25	Present	6000	None	0.7	Transparent, rather hard, very tough
8	60	Absent	6100	None	2	Rather soft, odor of dimer
9	62	Absent	1	1.5% Benzoyl peroxide	1	Product variable
10	62	Present	1	0.5% Benzoyl peroxide	1	Strong, tough, colorless
11	25	Absent	1	0.1% Catechol		Still fluid after 65 days
12	25	Present	1	1.6% Thiodiphenylamine		Still fluid after 13 months; strong odor of dimer

incomplete after twelve months. From some recent studies of the behavior of isoprene<sup>20</sup> it appears that the active catalyst in such transformations is a volatile peroxide. Since it is practically impossible to prepare a sample of chloroprene without exposing it to air at some time during the course of its preparation, it seems probable that even the products distilled in high vacuum are not altogether free from catalyst.

The amount of oxygen necessary to produce an optimum catalytic effect is quite small. At ordinary temperatures the presence of a volume of air equal to about 10% of the volume of the chloroprene sample causes the transformation to  $\mu$ -polymer to be completed in about eight to ten days. If the volume of air is much smaller than this the time required for the transformation is somewhat greater, but much larger ratios of air or oxygen do not greatly increase the velocity. Large quantities of oxygen do, however, affect the character of the final product. In general they lead to a product which, instead of being colorless or only slightly yellow, is dark brown and considerably harder and stiffer than the usual products.

Peroxides such as benzoyl peroxide also function as catalysts. Their use, however, presents no practical advantages, and is in fact somewhat hazardous. In samples containing benzoyl peroxide there is frequently a considerable induction period, and then reaction suddenly starts at some point in the sample and spreads very rapidly through the mass. The heat of reaction may be sufficient to char the sample.

The rate of formation of  $\beta$ -polychloroprene is not appreciably accelerated by oxygen or peroxides.

<sup>20</sup> Conant and Peterson, private communication

(b) **Temperature, Pressure and Light.**—Catalytic and anticatalytic effects in the polymerization of chloroprene are very powerful and difficult to regulate exactly; for this reason it is impossible to obtain precise quantitative correlations concerning the effect of temperature, pressure and light on the reaction velocity. It appears, however, that in the presence of air the transformation of chloroprene into the  $\mu$ -polymer occurs about four times as fast at  $62^\circ$  as at  $25^\circ$ . Thus the temperature coefficient of the catalyzed reaction is abnormally low. The relative rate of the formation of  $\beta$ -polymer, which is negligible at ordinary temperature, is more strongly affected by rise in temperature. Polymers produced at temperatures above  $50^\circ$  contain appreciable proportions of  $\beta$ -polymer. These proportions are still further increased if the reaction is carried out in the absence of air since this greatly reduces the speed with which  $\mu$ -polymer is formed without affecting the formation of  $\beta$ -polymer. In the absence of air the effect of increased temperature on the rate of transformation of chloroprene into  $\mu$ -polymer appears to be much greater than in the presence of air.

When chloroprene is polymerized at temperatures above  $80^\circ$  (in the absence of solvents) considerable decomposition occurs with liberation of appreciable amounts of hydrogen chloride, and the product is dark in color and tarry in consistency.

At a pressure of 6000 atmospheres the polymerization of chloroprene occurs about ten times as rapidly as at ordinary pressure.

Light has a considerable accelerating effect on the transformation of chloroprene into the  $\mu$ -polymer. The rate of formation of  $\beta$ -polymer is not affected. The active wave lengths lie in the blue, violet, and near ultraviolet.

(c) **Inhibitors.**—Substances that generally function as antioxidants act as powerful inhibitors for the transformation of chloroprene into the  $\mu$ -polymer. Under ordinary conditions a sample of chloroprene will set in four days to a stiff jelly containing about 40% polymer but the presence of 0.1% of catechol will permit the sample to remain fluid for several months. This fact confirms indications already mentioned that the spontaneous transformation of chloroprene into  $\mu$ -polymer is normally dependent upon the presence of traces of autoxidation products of the chloroprene. The formation of  $\beta$ -polymer is not thus dependent upon oxidation. Samples of chloroprene containing inhibitors, after several months at the ordinary temperature, are found to contain several per cent. of  $\beta$ -polymer, and frequently they are quite free of  $\mu$ -polymer. A sample of chloroprene containing 0.2% of pyrogallol yielded 49% of crude  $\beta$ -polymer after being heated for forty days at  $62^\circ$ .

The following types of compounds generally function as inhibitors: phenols, quinones, amines, mercaptans, thiophenols, aromatic nitro com-

pounds, halogens. Some compounds in each of these classes function as powerful inhibitors, others have a feebler effect. It is somewhat surprising to find aromatic nitro compounds in this list. Trinitrobenzene is among the most powerful of the inhibitors.

In the presence of relatively feeble inhibitors or small amounts of the more powerful inhibitors the polymerization of chloroprene can be effected at a somewhat diminished rate. The non-volatile polymer formed under these conditions, however, differs very considerably in its properties from that formed in the absence of inhibitors.

(d) **Solvents.**—The polymerization of chloroprene can be effected in the presence of solvents. If the solvent is one such as benzene, toluene, ethylene chloride, or carbon disulfide that powerfully swells  $\mu$ -polychloroprene, the resulting polymer remains dissolved. The polymerization of solutions containing as much as 50% by volume of chloroprene leads to the formation of stiff jellies. Even as little as 10% of chloroprene leads to highly viscous solutions. The solutions are generally colorless and transparent. The polymers contained in these solutions are somewhat different in their properties from the  $\mu$ -polychloroprenes produced under ordinary conditions. They are softer, and unless the solution is very old they can usually be redissolved in benzene.

The presence of the solvent considerably diminishes the rate of the polymerization, and dilute solutions polymerize more slowly than concentrated ones. Solvents also frequently exert a specific effect. Chloroprene dissolved in benzene polymerizes very much more rapidly than chloroprene dissolved in ether or pyridine.

Chloroprene may also be polymerized in the presence of non-volatile solvents, inert fillers and foreign materials of various kinds.

**Granular Polymer ( $\omega$ -Polymer).**—The polymerization of chloroprene occasionally leads to a coherent mass of glistening, hard, rubbery granules or globules ( $\omega$ -polymer). This material is non-plastic and it shows scarcely any tendency to imbibe solvents. The conditions favoring its formation are not very clearly understood, since it occasionally appears under the most diverse conditions. It seems certain, however, that its formation is autocatalytic. When a speck of this polymer appears in a sample of chloroprene during the early stages of its polymerization the granular growth continues to spread through the whole sample. Because of its cell-like structure it occupies more volume than the same amount of  $\mu$ -polymer, and if the growth begins to spread laterally through a sample it may burst the walls of a heavy Pyrex container even when the total volume of the container is much greater than the volume of the product. The presence of metallic sodium especially favors the formation of the granular polymer. It frequently appears under other conditions that result in very slow polymerization.

According to experiments made by H. W. Starkweather the formation of the  $\omega$ -polymer is initiated (or accelerated) by light of 3130 Å. wave length. The following observation is especially interesting.

Chloroprene containing pyrogallol to inhibit polymerization was placed in the bottom of a long Pyrex tube. The chloroprene was cooled to  $-80^\circ$ , and the tube was evacuated and sealed off. The lower half of the tube was covered with black friction tape to exclude light and the upper part was exposed to light from a mercury arc. During the exposure the lower part of the tube was kept in a bath at  $10^\circ$ ; the upper half was at  $60-65^\circ$ . After twelve hours there was a white deposit at the top of the tube. This deposit gradually increased during two and one-half days. Exposure to the light was then discontinued. The solid deposit, however, continued to form at the top of the tube as a white, crinkly mass, until the liquid in the bottom of the tube was completely exhausted.

It is interesting to observe that products similar to this granular polymer have been obtained from other dienes. Kondakow<sup>21</sup> observed that dimethylbutadiene in a closed flask in diffused daylight is gradually transformed into a white, insoluble mass, and Harries<sup>22</sup> obtained a similar product by the action of ultraviolet light on isoprene.

The great resistance of the  $\omega$ -polychloroprene as compared with the  $\mu$ -polymer to the swelling action of solvents indicates a considerably higher degree of cross-linking of the chains in the  $\omega$ -compound. If such a cross-linking should occur in a sufficiently regular fashion, it would lead to a three-dimensional primary valence lattice, a type of structure which is illustrated by the diamond, but is not known among synthetic organic compounds. The conditions under which the  $\omega$ -polymer is formed are such as might be especially favorable to the development of a regular three-dimensional structure. The formation of  $\omega$ -polymer is catalyzed by an  $\omega$ -polymer surface; the process is one of heterogeneous autocatalysis. It seems most probable that the function of the  $\omega$ -polymer surface in this connection is not (or at least not wholly) to activate adsorbed molecules of the monomer, but rather to orient the adsorbed molecules into a configuration favorable for mutual union. The incidence of activating energy could then bring about the combination of a very large number of molecules in a single act.

As a matter of fact the granular polymer at first sight gives the impression of being definitely macrocrystalline, but on closer observation the crystals turn out to be globules. x-Ray examination gives only an amorphous pattern.

It is interesting to note that the granular polymer never appears in samples of  $\alpha$ -polychloroprene (described later) that contain phenyl- $\beta$ -naphthylamine.

<sup>21</sup> Kondakow, *J. prakt. Chem.*, [2] 64, 109 (1901).

<sup>22</sup> Pummerer and Koch, *loc. cit.*, p. 268.

**Progressive Changes during the Spontaneous Polymerization of Chloroprene.**—The following table illustrates in more detail the changes in properties and composition that occur when a sample of chloroprene is allowed to stand under ordinary conditions in the presence of a little air.

TABLE II  
CHANGES DURING THE POLYMERIZATION OF CHLOROPRENE

Time, days	Polymer, %	Density	Viscosity in centipoises
0	0	0.952	0.4
1	4	..	6.0
2	14	0.98	550.0
4	45	1.06	Stiff jelly
10	99+	1.23	Non-plastic

The polymer formed during the early stages of the reaction can be isolated by precipitation with alcohol, or by distilling off the unchanged chloroprene *in vacuo*. This material is very different in its properties from the final product, the  $\mu$ -polychloroprene already described. It is soft, plastic, and completely soluble in benzene. We call this plastic polymer  $\alpha$ -polychloroprene. When allowed to stand at the ordinary temperature it slowly reacts with itself and in the course of a day or two is transformed into a product apparently identical with the  $\mu$ -polymer.

**Mechanism of the Formation of  $\alpha$ - and  $\mu$ -Polymers.**—The isolation of the  $\alpha$ -polymer demonstrates that the transformation of chloroprene into the  $\mu$ -polymer is a step-wise reaction. Some of the facts concerning the two polymers and their relation to each other are best correlated by a brief discussion of mechanism.

The transformation of chloroprene into the  $\alpha$ -polymer is evidently a chain reaction. It is enormously susceptible to catalytic and anticatalytic effects; it is accelerated by light; and although a large number of molecules is combined to form a single larger molecule, the apparent order of the reaction is low. The reaction probably first involves the coupling of an activated molecule of chloroprene with another chloroprene molecule. The activating energy persists in the polymeric chain until it has been built up to a considerable length. The molecules of  $\alpha$ -polymer thus formed doubtless have the linear structure already suggested in formula XIII. The formation of a molecule of  $\alpha$ -polymer involves a series of separate acts, but these follow one another in very rapid succession. Under ordinary conditions the  $\alpha$ -polymer present when 4% of a sample of chloroprene has polymerized is indistinguishable from the polymer present when 20% of the chloroprene has polymerized.

The transformation of the  $\alpha$ -polymer into the  $\mu$ -polymer consists in the cross-linking of the long chains into a three-dimensional structure of the type represented in formula XIX. In a sample of chloroprene undergoing spontaneous polymerization this process becomes noticeable when

the concentration of polymer has reached about 25%. It is marked by an abrupt change in properties. The viscosity increases very rapidly and the sample soon sets to a stiff jelly. If the polymer is isolated just before this point is reached, it is found to be soft and plastic. Polymer isolated just after this abrupt change is still soft, but the manner in which it resists permanent deformation indicates the presence of a considerable proportion of the  $\mu$ -polymer.

The reactions, (1) chloroprene  $\longrightarrow$   $\alpha$ -polymer, and (2)  $\alpha$ -polymer  $\longrightarrow$   $\mu$ -polymer, are not merely two stages of a single process, but are different reactions. The polymerization of chloroprene is rather strongly inhibited by primary aromatic amines, such as aniline, the naphthylamines, and benzidine; but these same compounds when mixed with isolated  $\alpha$ -polymer accelerate its conversion into  $\mu$ -polymer. The temperature coefficients of the two reactions are different. For reaction (2) the ratio of the velocity constants for a temperature increase of  $10^{\circ}$  is about two; for reaction (1) the ratio is considerably less than two.

**Other Polymers; Balata-like Polymer.**—The  $\alpha$ -,  $\mu$ - and  $\omega$ -types are not chemical individuals but rather qualitatively different species of polymeric mixtures. The properties of each type may vary over a considerable range and in practice no doubt one generally has to do not with a pure species but with a mixture in which one of the species may preponderate. A consideration of the formulas assigned to the  $\alpha$ - and  $\mu$ -polymers will suggest some of the complications that might arise. The molecules of the  $\alpha$ -polymer are no doubt chains of very great length, but in the polymerization of chloroprene under certain conditions, *e. g.*, at elevated temperature, the process of cross-linking may set in before the chains have attained the usual length of  $\alpha$ -polymer chains. One will then have a product very different in its properties from that produced by the vulcanization of  $\alpha$ -polymer. Stereochemical factors (*e. g.*, *cis-trans* isomerism) may also produce great variations in the character of the products.

The  $\alpha$ -,  $\beta$ -,  $\mu$ - and  $\omega$ -polymers by no means exhaust the different types of polychloroprenes. Anything that influences the velocity of the polymerization has some effect on the properties of the product, and the modifications produced by inhibitors and catalysts are especially marked. The phenomena in this connection are very complex. It would be useless to attempt to recognize as distinct species all the distinguishably different polymeric products derived from chloroprene.

There is, however, one type of product that appears to be qualitatively different from the  $\alpha$ -,  $\beta$ -,  $\mu$ - and  $\omega$ -polymers. This material rather closely resembles balata in its properties. It is obtained more or less contaminated with the other types of polymers under various conditions, but especially by the polymerization of chloroprene in the presence of inhibitors such as iodine or the tetraalkyl thiuramdisulfides.

A typical specimen of this balata-like material when cold is a hard, amorphous, non-brittle mass. When warmed to  $60^{\circ}$  it becomes soft and plastic. At higher temperatures it is quite sticky. When heated under vulcanizing conditions the plasticity is partly lost, but the transformation to the elastic condition is very incomplete. We make no attempt to suggest a structure for this material.

**Conditions for the Isolation of  $\alpha$ -Polymer.**—Owing to the effect of changing concentrations, the rate of formation of  $\alpha$ -polymer progressively decreases during the polymerization of chloroprene, and the rate of the conversion of  $\alpha$ -polymer into  $\mu$ -polymer progressively increases. For this reason if pure  $\alpha$ -polymer is to be obtained, the reaction must be interrupted before all of the chloroprene has polymerized.

Under the most favorable conditions the concentration of the  $\alpha$ -polymer in the polymerizing mixture can be built up to 30 or 40% before any appreciable transformation to  $\mu$ -polymer occurs. The reaction is best conducted in glass vessels under strong illumination from a Mazda lamp or a mercury arc in glass. The most effective wave lengths lie in the long ultraviolet, but the use of a quartz container with mercury arc radiation is not advisable on account of the danger of forming granular polymer. The temperature should be kept in the neighborhood of  $35^{\circ}$ . Under these conditions about 30% of the chloroprene is polymerized in sixteen to twenty-four hours. The product is a thick, colorless, transparent sirup. If this sirup is poured into a large volume of alcohol, the  $\alpha$ -polymer separates as a colorless mass and the unchanged chloroprene remains dissolved in the alcohol. The  $\alpha$ -polymer can also be separated by allowing the unchanged chloroprene to distil out of the mixture under diminished pressure. The mixture is preferably stirred during the distillation.

**Properties of the  $\alpha$ -Polymer.**—In density and refractive index the  $\alpha$ -polymer lies very close to the  $\mu$ -polymer. The  $\alpha$ -polymer resembles milled smoked sheets in its physical properties and mechanical behavior. It is plastic and it dissolves completely in benzene to form highly viscous solutions. It can be calendered into thin sheets or extruded with the usual rubber machinery.

At  $30^{\circ}$  the  $\alpha$ -polymer loses its plastic properties and becomes completely changed to the elastic form ( $\mu$ -polymer) in about forty-eight hours. At  $130^{\circ}$  the transformation is complete in about five minutes. This process corresponds to the vulcanization of natural rubber, but sulfur is not needed and when present it takes no part in the process. The speed of this transformation can be greatly modified by the addition of various substances, some of them materials that are used in the vulcanization of natural rubber.

Zinc oxide brings about the vulcanization of  $\alpha$ -polymer in eight to ten hours at  $30^{\circ}$ . Zinc chloride, zinc butyrate and ferric chloride are even

more active catalysts. The most effective organic catalysts are primary aromatic amines such as aniline, the naphthylamines and benzidine. Diphenylguanidine, which is a relatively active vulcanization accelerator for natural rubber, is a mild accelerator for  $\alpha$ -polymer. On the other hand, mercaptobenzothiazole and tetraalkylthiuram sulfides, which are active natural rubber accelerators, have no accelerating action on the  $\alpha$ -polymer. Basic inorganic materials such as lime and magnesium oxide, which may accelerate natural rubber through their action with sulfur, have a slight retarding influence on the vulcanization of  $\alpha$ -polymer. Strong acids and acidic materials that retard the vulcanization of natural rubber have no influence on the curing of plastic polymer.

Secondary aromatic amines such as phenyl- $\beta$ -naphthylamine powerfully inhibit the vulcanization of  $\alpha$ -polymer at ordinary temperature. This fact is of considerable practical importance since it brings about the possibility of storing the plastic polymer over long periods of time. The phenyl- $\beta$ -naphthylamine also acts as an antioxidant and confers age-resisting properties on the final product. The inhibiting effect of the phenyl- $\beta$ -naphthylamine on the curing of the  $\alpha$ -polymer largely disappears above 100°.

**Behavior of  $\alpha$ -Polymer in Compounding and Properties of the Cured Rubber.**—The compounding ingredients that can be used with  $\alpha$ -polymer are similar to those used with natural rubber, but there are a number of important additions. Materials such as ground leather and cork which strongly retard the vulcanization of natural rubber act as inert ingredients in  $\alpha$ -polymer. Carbon black and zinc oxide act as reinforcing agents as they do in natural rubber and impart good abrasion resistance. In contrast to their action in rubber, whiting and clay are perfectly wet by  $\alpha$ -polymer, and they produce compounds having good tear resistance. Cotton and other vegetable fibers are also much more perfectly wet by  $\alpha$ -polymer than by rubber. Most plasticizing and softening materials such as mineral oil, stearic acid and pine tar are insoluble in  $\alpha$ -polymer and have little true softening action. Milling also produces little softening other than a temporary thermal effect. Mineral rubber and similar asphaltic materials act as diluents with little effect on the physical properties of the vulcanized material.

Natural rubber can be successfully milled into  $\alpha$ -polymer, although there is little affinity between the two. Sheets of the two rubbers before vulcanization may be firmly pressed together and easily separated. A reasonably firm union can be obtained between natural and chloroprene rubber when they are vulcanized together under sufficient pressure. Benzene solutions of rubber and  $\alpha$ -polymer are not compatible; when thoroughly mixed they quickly separate into two layers.

Table III gives the composition of compounded stocks prepared from

$\alpha$ -polychloroprene and from smoked sheets. These were used for a series of parallel tests to compare the behavior of the two rubbers. All the processing and testing were carried out with the usual rubber laboratory equipment.

TABLE III  
COMPOSITION OF COMPOUNDED STOCKS FROM  $\alpha$ -POLYCHLOROPRENE AND FROM SMOKED SHEETS

Materials	Amount in grams	Compound from $\alpha$ -polychloroprene	Compound from smoked sheets
$\alpha$ -Polychloroprene	100	...	
Smoked sheet rubber	...	100	
Zinc oxide	10	10	
Sulfur	...	3	
Stearic acid	2	2	
Diphenylguanidine	...	1	
Benzidine (accelerator)	0.5	..	
Phenyl- $\beta$ -naphthylamine	1	1	

The effect of different times and temperatures of vulcanization on the physical properties of the two compounds is shown in Table IV. The chloroprene rubber reaches a maximum tensile strength after only five minutes at 140°; but the strength is not adversely affected if the curing time is extended to sixteen hours. In contrast to this, the natural rubber compound vulcanizes more slowly and softens rapidly under the action of prolonged vulcanization. The maximum tensile strength for the chloroprene compound is slightly lower than that for the natural rubber compound. In contrast to the smoked sheet compound the chloroprene compound shows no reversion and the load supported at 500% elongation continues to increase slowly throughout the curing range. When the

TABLE IV  
EFFECT OF VULCANIZATION ON PHYSICAL PROPERTIES OF COMPOUNDED STOCKS

Vulcaniza- tion temp., °C.	Minutes vulcaniza- tion time	Load at 500% elongation, kg. per sq. cm.	Chloroprene rubber	Smoked sheet	Tensile strength at break, kg. per sq. cm.	Chloroprene rubber	Smoked sheet	% Elongation at break	Chloroprene rubber	Smoked sheet
110	20	16.0	..	..	166.9	..	..	920	..	..
110	40	28.1	..	..	177.5	..	..	860	..	..
120	20	28.2	..	..	169.8	..	..	860	..	..
120	40	30.2	..	..	171.2	..	..	820	..	..
140	5	29.9	..	..	170.5	..	..	825	..	..
140	10	33.4	..	..	170.5	..	..	780	..	..
140	15	38.6	12.2	..	172.2	12.6	..	770	860	..
140	20	38.6	16.0	..	170.5	15.2	..	760	830	..
140	30	42.2	21.0	..	172.2	175.0	..	750	820	..
140	60	42.2	35.1	..	167.0	210.0	..	750	760	..
140	90	43.9	46.2	..	167.0	192.0	..	720	680	..
140	120	45.7	42.0	..	181.0	205.0	..	740	720	..
140	480	54.4	14.0	..	165.2	87.0	..	700	800	..
140	960	63.3	11.9	..	151.1	82.1	..	640	820	..

polychloroprene compound is heated longer than sixteen hours at 140° a material resembling hard rubber is formed.

The chloroprene compound is very resistant to the action of ozone. The two compounds were stretched about fifteen per cent. and exposed to ozone-containing air. The natural rubber compound was ruptured in three minutes; the chloroprene compound was not detectably affected during an exposure of three hours.

Table V shows the results of artificial aging tests on the two compounds of Table III. The chloroprene compound was cured for fifteen minutes and the natural rubber compound for sixty minutes at 140°. The tests were carried out at 70° in oxygen at twenty atmospheres. Under these conditions twenty-four hours is generally considered to approximate one year of natural aging for rubber. These data indicate that the chloroprene rubber is considerably more resistant to oxidation than natural rubber. Natural aging tests have not been carried out for a length of time sufficient to confirm this conclusion, but samples of the chloroprene rubber compound that have been kept for one year show no deterioration.

TABLE V  
AGING PROPERTIES OF COMPOUNDS FROM SMOKED SHEETS AND FROM  
 $\alpha$ -POLYCHLOROPRENE

Days in oxygen bomb at 70°	Tensile strength, kg. per sq. cm.		% Elongation at break	
	Chloroprene rubber	Smoked sheets	Chloroprene rubber	Smoked sheets
0	172.2	232.0	890	720
1	212.6	195.0	845	680
2	181.0	163.4	820	660
3	193.8	159.9	805	670
8	209.1	116.1	720	595
14	165.2	54.5	690	510

Chloroprene rubber is much more resistant than the natural product to the action of solvents and many chemicals. After seventy-two hours the chloroprene compound had increased 7% in weight by immersion in light machine oil and 25% by immersion in kerosene, and it had retained more than half of its original tensile strength in each case. The tensile strength of the natural rubber was destroyed under these conditions. In contrast to natural rubber, chloroprene rubber is not attacked by hydrogen chloride, hydrogen fluoride, sulfur chloride, ozone and many other chemicals. The high chlorine content of the chloroprene rubber also renders it very resistant to combustion. Measurements of diffusion of both hydrogen and helium through a polychloroprene membrane show it to be only 40% as permeable as natural rubber. The absence of water-soluble materials in chloroprene rubber makes it very resistant to penetration by water.

**Synthetic Latex.**—Chloroprene is readily emulsified by shaking or

stirring it with water containing an emulsifying agent such as sodium oleate. The resulting emulsion polymerizes very rapidly and completely. The polymer remains suspended or emulsified and constitutes an artificial latex. When the water is allowed to evaporate from a layer of this latex, a thin coherent, strong, elastic film remains. This film in its physical and mechanical properties very closely resembles the  $\mu$ -polychloroprene already described: it is strong, extensible, elastic, resilient, non-plastic and not thermoplastic, and it is swelled but not dissolved by benzene.

The following example illustrates the preparation of a synthetic latex. Four hundred grams of chloroprene is slowly added with vigorous stirring to 400 g. of water containing 8 g. of sodium oleate in a wide-mouthed bottle. A smooth emulsion results. After a time (usually about thirty minutes) the temperature of the mixture begins to rise and it may quickly reach the boiling point of the chloroprene unless cooling is applied. After standing for two to eight hours at room temperature the polymerization is complete. The mixture is then practically odorless.

More uniform products are obtained if the temperature is carefully controlled during the emulsification and polymerization. At a temperature of  $10^{\circ}$  the process is complete in about twenty-four hours—always in less than forty-eight hours. The reaction is always characterized by an induction period, which at  $10^{\circ}$  usually lasts forty to sixty minutes. It is evident that the speed of polymerization of chloroprene is much greater (apparently at least 20-fold) in emulsion than otherwise. The particular nature of the interface appears to be of great importance in determining the rate of polymerization. The rate is much more rapid with sodium oleate than with egg albumen although both of these emulsifying agents produce very small particles.

A small amount of free acid is developed during the polymerization of the emulsions, and this gradually brings about coagulation during storage. However, if a little ammonia (e. g., 5 g. of  $\text{NH}_3$  per liter) is added to the latex after completion of the polymerization this tendency is avoided. Latex stabilized in this way can be stored indefinitely without change. In addition to the ammonia it is ordinarily desirable to add an antioxidant such as phenyl- $\beta$ -naphthylamine since this greatly prolongs the life of articles prepared with the latex.

The particle size of latex prepared according to the above example is very small and remarkably uniform. Figure 4 gives the results of some measurements made by J. B. Nichols with the ultracentrifuge. When sodium oleate is used as the emulsifying agent the mean radius of the particles is about  $0.063\mu$  and more than 60% of the particles lie between 0.05 and  $0.07\mu$ . It appears that the ultracentrifugal method has not been applied to natural latex, but according to Hauser<sup>23</sup> the latex from

<sup>23</sup> Hauser, *Latex*, Theodor Steinkopff, Leipzig, 1927, p. 56.

mature *Hevea* trees contains particles ranging in diameter from 0.5 to  $3\mu$  as well as a considerable proportion of smaller particles. The particle size of the synthetic latex can be controlled to a certain extent by suitably modifying the nature and the amount of the emulsifying agent. The use of lithium oleate in the ratio of two grams to one hundred grams of chloroprene gives particles having a mean radius of about  $0.087\mu$ .

In the preparation of the synthetic latex the ratio of chloroprene to water can be varied over a wide range. As long as the concentration lies below 55% by weight of polychloroprene, the latices are very fluid. Above this concentration there is a sharp increase in viscosity, and a 60% latex is quite thick.

The synthetic latex is rapidly coagulated by acids, alcohol, acetone and many salts. The polychloroprene separates as a coherent mass, which is at first quite soft and plastic. However, as soon as the water is squeezed out, this plasticity is lost. The mass then has the properties already indicated for  $\mu$ -polychloroprene—it is analogous to a soft, vulcanized natural rubber.

**Applications of the Latex.**—The chloroprene latex can be directly applied to many uses after the manner of vulcanized natural latex. In this connection it has some special advantages owing to its peculiar properties. Thus on account of its small particle size it penetrates porous articles such as leather and wood in a manner that can hardly be approached with natural latex.

Shaped articles are readily prepared by dipping forms of glass, metal or porcelain into the latex and coagulating the resulting film or allowing it to dry. By repeated dipping, articles of any desired thickness can be built up.

The latex can be mixed with dyes, fillers and modifying and protective agents of various kinds to adapt it to specific uses.

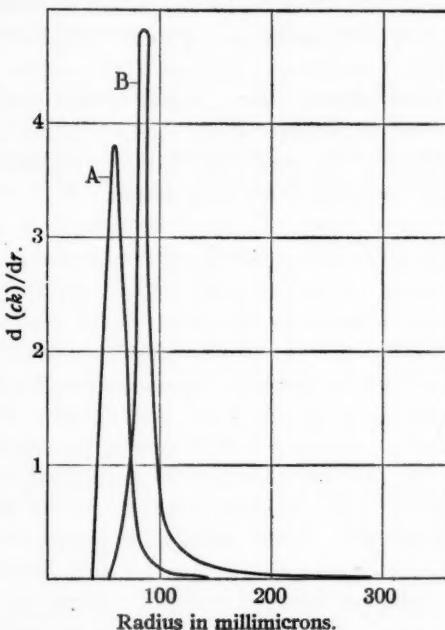


Fig. 4.—Weight distribution curve for chloroprene latices. The units are such that the area under the curves for any radius interval equals the fraction of the total weight of particles whose radii lie in that interval. Curve A, latex made with sodium oleate. Curve B, latex made with lithium oleate.

**Polymerization of Chloroprene in Porous Materials.**—Attempts to impregnate such porous materials as leather, wood and tile with natural rubber are unsuccessful, whether the rubber is used in the form of latex or dissolved in a solvent such as benzene; but a very intimate impregnation of these materials with chloroprene rubber can be accomplished by soaking them in chloroprene and then allowing the rubber to be formed in place. Chamois or kid leather saturated with its own weight of chloroprene and sealed to prevent evaporation until polymerization is complete becomes translucent and assumes a rubber-like flexibility without extensibility. Impregnated spruce becomes water resistant but its appearance is unchanged. This process may be used with any porous or bibulous material that does not contain inhibitors for the spontaneous polymerization of chloroprene.

**Conclusion.**—If space permitted it would be possible to review the literature on synthetic rubber from diene hydrocarbons and to show that almost every recorded peculiarity and complication in this field finds some analogy in the behavior of chloroprene. Chloroprene is therefore capable of serving adequately as a representative diene in studying as a scientific problem the synthesis of rubber-like materials, and for this purpose it has the great advantage of its very high speed of polymerization as compared with dienes previously available.

On the economic side the greatly diminished costs of producing natural rubber have obviated the need for an artificial material having the same properties. There remains, however, the need for a synthetic rubber that is free from some of the inherent defects of the natural product. The differences between polychloroprene and natural rubber are sufficient to suggest considerable potentialities for the new synthetic product.

### Summary

Chloro-2-butadiene-1,3 (chloroprene) is described and its structure established through reactions leading to its conversion into butane- $\alpha$ ,  $\beta, \gamma, \delta$ -tetracarboxylic acid, and into  $\beta$ -chloroanthraquinone.

Within ten days under ordinary conditions in a closed vessel containing a little air, chloroprene spontaneously changes into a transparent, resilient, strong, non-plastic, elastic mass resembling vulcanized rubber. This product is called  $\mu$ -polychloroprene. By interrupting the polymerization before it has proceeded to completion one obtains a soft, plastic product ( $\alpha$ -polymer) that resembles unvulcanized rubber. Under the action of heat the  $\alpha$ -polymer rapidly changes to the  $\mu$ -polymer. Other polymers of chloroprene described are volatile ( $\beta$ -) polymer, granular ( $\omega$ -) polymer, and balata-like polymer. The structures of the polymers are discussed as well as the effect of conditions on the formation of each type.

Unlike any previously described synthetic rubbers,  $\mu$ -polychloroprene

resembles natural rubber in the fact that when it is stretched its x-ray diffraction pattern shows a point diagram.

The transformation of chloroprene into  $\mu$ -polychloroprene occurs very rapidly in aqueous emulsion. The resulting product constitutes a synthetic (vulcanized) latex. It has a much smaller particle size than natural latex and it penetrates porous materials more readily.

Chloroprene can also be polymerized in the pores of porous or bibulous materials. The materials thus become intimately impregnated with synthetic rubber.

Compared with natural rubber the new synthetic rubber is more dense, more resistant to absorption or penetration by water, less strongly swelled by petroleum hydrocarbons and less permeable to many gases. It is much more resistant to attack by oxygen, ozone, hydrogen chloride, hydrogen fluoride and many other chemicals.

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## X-Ray Study of Rubber Structure

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IT IS SHOWN by x-ray diffraction methods that a time interval is required to build up a fiber structure in stretched rubber. Four rather obvious types of explanation for this effect are pointed out, and serious objections to three of these are mentioned. The most probable explanation seems to be that time is required either to squeeze out unfavorably oriented molecules to the interfaces of fibers made up of favorably oriented molecules; or to pull out, in the direction of fiber-orientation, tangled portions of molecules. Such a picture would cause the easily stretched, favorably oriented molecules to assume the role usually played by the more solid phase of a gel, and would cause the less favorably oriented molecules (or portions of molecules) to play the part ordinarily played by the liquid phase of a gel.

SINCE the outstanding properties of rubber are those of a colloidal gel, it would seem reasonable at first sight to picture it as having the two-phase structure found for ordinary jellies. The chemical data in the literature do not seem to be in entire accord with such a simple picture, and even the published x-ray work on stretched rubber is capable of more than one simple interpretation. It has therefore seemed worth while to carry out additional x-ray experiments of a somewhat different type on the ultimate structure of rubber.

## REVIEW OF PREVIOUS WORK

It will facilitate the discussion of the new data presented here if the results of work so far reported in the literature are first outlined briefly. These results<sup>1</sup> may be classified in the following manner: the existence and mutual transformation of different polymers in rubber; and data concerning the physical structure as determined from x-ray diffraction patterns.

**EXISTENCE OF POLYMERS IN RUBBER.** The existence of two different constituents in rubber was assumed by many of the early workers in the field. The first workers include Govi (10) who in 1867 assumed that rubber is analogous to a solid foam. His work was shortly disproved, however, by Thomas (25) and later by Hehesus (15). Theories based on the presence of two constituents in rubber have been set forth by many workers, including Malock (20), Fessenden (7), Breuil (9), Chaveau (4), Schwarz and Kemp (24), and Cheneveau and Heim (5). There have also been many attempts to separate the constituents of rubber. Weber (27) and Caspari (3) were the first to attempt the fractionation of rubber into hydrocarbons of different properties. This has been successfully accomplished by Duclaux (6), Feuchter (8), and Pummerer (23). These hydrocarbons were shown to have the empirical formula  $C_4H_8$ , but exhibited entirely different degrees of polymerization. The more soluble polymers have been designated as alpha rubber, and the more insoluble resinous forms as beta rubber. It is doubtful if any sharp dividing line can be drawn between different groups of polymers. In recent years a number of investigators, including Pickles (22), Lunn (19), Freundlich and Hauser (9), Van Rossem (26), Park (21), Hauser (11), and others, have conducted investigations on the structure of rubber, based on the properties which it would possess if it consisted of such polymers. Further experiments by Bary and Fleurent (1) and others have been interpreted as showing that these polymers are mutually transformable, that in ordinary rubber there is an equilibrium value for the relative amounts of the various polymers present, and that this equilibrium can be disturbed by aging, heating, etc.

From the foregoing data it will be seen that there is much evidence in favor of the existence of analogous substances in rubber whose physical properties differ to a considerable extent. For information regarding the structure of these substances in ordinary rubber, it is necessary to turn to x-ray data.

**X-RAY DETERMINATIONS.** X-ray experiments by Katz and Bing (16, 17, 18) showed in 1925 that, when a beam of x-rays

<sup>1</sup> Excellent reviews of the work on the composition and structure of rubber have been published by Hauser and Bary [*Rubber Age (N. Y.)*, 29, 685-8 (1928)], and by G. L. Clark [*Indian Rubber World*, 79, 559 (1929)]. The present summary is limited to those articles which seem to have a direct bearing on the present work.

from a pinhole slit impinges on normal unstretched rubber, the only diffraction is that characteristic of amorphous substances; *i. e.*, the diffraction pattern shows only diffuse uniform rings of low intensity. They found, however, that, when the substance was sufficiently stretched, the diffraction rings changed in intensity from point to point so that they tended to appear as small areas or "diffraction spots," thus giving diffraction patterns characteristic of fibrous materials. These diffraction spots disappear when the tension on the rubber is released, or when the rubber is heated.

Hauser and Mark (13) confirmed the work of Katz and Bing, and showed that excessive elongations (1000 per cent) do not change the positions of the diffraction spots but do increase their intensity. The percentage of elongation in the rubber at which the diffraction spots appear depends upon the rate of stretching (14). If raw rubber is stretched slowly enough, diffraction spots will not appear even at 500 per cent elongation.

Hauser and Mark at first explained these results by assuming that unstretched rubber is made up of two types of material, one of which is "dissolved" in the other. These may be thought of as being the two groups of polymers mentioned by Bary and Fleurent (1). It was further assumed that, in the unstretched rubber, crystalline aggregates or fibers of the higher polymers (beta rubber) exist, but that they are swollen and distorted by the presence of the lower polymers (alpha rubber) and do not therefore give rise to a diffraction pattern. By quickly stretching the rubber, however, the alpha rubber is expelled, leaving the regularly oriented crystalline aggregates of beta rubber which are responsible for the x-ray diffraction pattern.

Later Hauser (12) modified this theory somewhat by assuming that rubber consists of long helical parallel chains of isoprene molecules which unwind during stretching. The "coiled-spring" type of molecule would not give a diffraction pattern, but in the stretched position the symmetry would be such as to give a diffraction pattern. This theory does not necessitate the postulation of a number of polymers in rubber despite the chemical evidence, but, on the other hand, it does not require that such a postulate be abandoned. It would seem to be a corollary to such a picture that, when a strip of rubber is stretched, not only is it necessary to pull out some of the helical molecules into straight chains, but it would be necessary to push aside the other molecules to the fiber interfaces in order that the straight chains should not be warped. The regularly oriented straight chains would then be capable of giving rise to the observed diffraction patterns.

If this last theory is correct, it would be expected that a time interval would be required after stretching before rubber could show evidence of crystallinity. This interval would represent the time required for those molecules which were not oriented along the direction of stretch to leave the oriented

fibers and travel to the fiber-boundary. It is the purpose of the present work to demonstrate the presence or absence of this time interval, thus bringing one step closer a tenable picture of the structure of rubber.

#### APPARATUS AND EXPERIMENTAL PROCEDURE

**APPARATUS.** A schematic diagram of the apparatus used is given in Figure 1.

A Coolidge x-ray tube, *A*, was used with a molybdenum target operating at a potential of 30,000 volts. After passing through the shutter system, *S* and *S*<sub>1</sub>, the K-beta radiation from the molybdenum target was filtered out with a zirconium filter, *F*. The x-ray beam was further defined by the holes, *S*<sub>2</sub> and *S*<sub>3</sub>, which were 1.6 mm. ( $\frac{1}{16}$  inch) in diameter. Scattered radiation from the holes was eliminated by allowing the beam to pass through a 6.4-mm. ( $\frac{1}{4}$ -inch) hole in the screen *S*<sub>4</sub>. The beam was diffracted by the rubber specimen, *R*, and the pattern was obtained on the film, *P*. The rubber was fastened between a fixed support, *M*<sub>1</sub>, and a movable support, *M*<sub>2</sub>. The latter

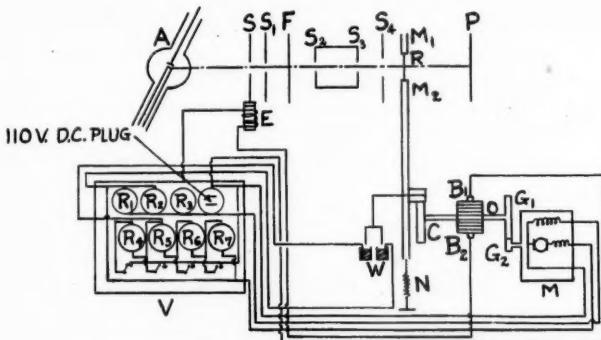


FIGURE 1. SCHEMATIC DIAGRAM OF APPARATUS

was held under tension by the spring, *N*, and was moved up and down by the action of the cam, *C*, which had a throw of 30 mm. ( $1\frac{3}{16}$  inches). The cam was so designed that the rubber was stretched rapidly to a position of maximum elongation and was held in this manner for one-half of a revolution of the cam, after which it was allowed to return rapidly to its original position, and the cycle was then repeated. A commutator, *O*, containing 21 segments, was mounted on the same shaft as the cam, and the two brushes, *B*<sub>1</sub> and *B*<sub>2</sub>, in contact with it were mounted at  $90^\circ$  to each other. These brushes and the windings of an electromagnet, *E*, were connected in series through a fixed resistance, *R*<sub>1</sub>, to a 110-volt source of potential as shown. By connecting together a portion of the segments of the commutator in the proper manner, the shutter, *S*, could be operated by the electromagnet in synchronism with the stretching of the rubber, so that the shutter was opened only when the rubber was in a position of maximum elongation. Also, by connecting different members of the commutator segments together, the shutter could be held open for different lengths of time, and the phase relation of this time to the stretching cycle could be controlled. The shaft on which the cam and commutator were mounted was turned by a motor, *M*, having a variable speed control, *V*. The motor was connected to the

shaft through a worm and gear arrangement,  $G_1$  and  $G_2$ , which reduced the speed of the shaft to one-fiftieth of that of the motor. The motor had a maximum speed of 1200 r. p. m., thus giving a maximum of 24 stretches of the rubber per minute. By means of the variable speed control, a minimum of approximately 4 stretches of the rubber per minute could be obtained. The variable speed control consisted of a number of lamp resistances,  $R_1, R_2, R_3, R_4, R_5, R_6, R_7$ , which could be connected in the motor circuit as shown in Figure 1.

Since previous work has shown that the intensity of the interferences is very markedly affected by the rate of stretching, it was desired to maintain a constant rate of stretching during all of the experimental work. By maintaining a constant rate of stretch, however, the time range over which the rubber could be held in a position of maximum stretch would be seriously limited. Therefore an automatic switching arrangement,  $W$ , was devised which consisted of a forked piece of copper fastened to the reciprocating shaft,  $M_2$ , operated by the cam,  $C$ , in such a way that during the period of maximum stretch it would make contact between the mercury wells indicated in Figure 1. This in turn altered the resistance in the motor circuit, thus changing the speed of the motor and hence the time of maximum stretch. The switch,  $W$ , slowed down the motor speed to any desired value at the instant when the rubber had reached a position of maximum stretch. This speed of the motor was

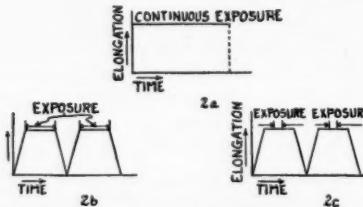


FIGURE 2. GRAPH OF STRETCHING

held at this value so long as the cam,  $C$ , held the rubber in a position of maximum stretch, but at the end of this period the switch broke contact and the motor resumed its original speed. When the rubber had again reached the position of maximum stretch, the cycle was repeated.

**PROCEDURE.** The samples of rubber used were 25 mm. long, 8 mm. wide, and 1.5 mm. thick. The ends were protected from abrasion by thin rubber facing strips, which were held in position on the sample by means of brass clamps. These clamps were attached directly to the ends of  $M_1$  and  $M_2$  of Figure 1. The length of the rubber strip between the clamps was kept constant. It was somewhat more than 6.4 mm.

Rapid reproducible stretching was obtained by means of the cam,  $C$ , of Figure 1, which was shaped so that the rate of stretching and the rate of relaxation were equal. In all of the work the time of stretching was 0.6 second. Since the amount of stretch was 30 mm. (420 per cent), the rate of stretching was approximately 50 mm. (i. e., 700 per cent) per second.

The rubber was held in a position of maximum stretch for  $180^\circ$  of each revolution of the cam. By means of the switch,  $W$ , of Figure 1 the time during which the rubber was held at

maximum stretch could be varied from 1.2 seconds to approximately 11 seconds.

The total time of exposure varied with the particular kind of rubber in use and with the percentage of elongation. With the kind of rubber used in the final experiments, 1 hour and 45 minutes were found to be sufficient. Since the shutter was open only a fraction of the time in most of the experiments, the total time of the run varied in length. The exposure was made at various parts of the cycle in order to determine what the time interval was (if any) between the time of stretching and the beginning of the fiber state. This is illustrated diagrammatically in Figure 2.

A large number of preliminary experiments was made, using ordinary vulcanized "inner tube" rubber. This was found to be unsatisfactory for the present purposes, partly because of the very great elongation necessary to obtain a diffraction pattern, and partly because of the presence of diffraction spots caused by the orientation of the  $MgCO_3$  used as a filler in the rubber. Pure rubber was likewise found to be unsatisfactory, owing to fatigue on continued stretching. The rubber which was used in the final experiments was vulcanized to give it the necessary toughness, but it contained only small amounts of inorganic fillers and had not been subjected to prolonged mechanical treatment, and therefore gave good diffraction patterns without excessive elongation. Its composition was as follows:

	<i>Parts</i>
Pale crepe	90.0
Mineral rubber	3.0
Sulfur	1.5
Accelerator	0.5
ZnO	2.5
Antioxidant	1.0

It had been milled on warm rolls for about 20 minutes.

#### INTERPRETATION OF RESULTS

It was found that an elongation of 380 per cent, maintained continuously (Figure 2a) gave a faint fiber diffraction pattern in 1 hour and 45 minutes. Then the stretching mechanism was operated so that the rubber was held at 380 per cent elongation for 11 seconds during each cycle, and the x-ray shutter was held open during the whole 11 seconds for each cycle (Figure 2b). No fiber diffraction pattern was found, although the total exposure time was made to total up to 1 hour and 45 minutes as before. No fiber diffraction pattern was found for a similar cyclic stretching of 400 per cent. A continuous stretch of 420 per cent gave a comparatively strong fiber pattern, in 1 hour and 45 minutes, and a weaker fiber pattern was obtained (film 100) with a cyclic stretching of 420 per cent when the x-ray shutter was held open for 11 seconds after stretching, the total exposure time being still 1 hour and 45 minutes. Then the rubber was stretched cyclically 420 per cent, and the shutter was kept open only 1.2

seconds after the end of each stretching cycle. No certain evidence of a fiber pattern could be found on the film, even though the total time of actual exposure was 1 hour and 45 minutes. This does not mean, of course, that no fibering had occurred during the first 1.2 seconds after stretching. It does mean, however, that any possible fibering was extremely small in amount when compared with the results of film 100 (see above). In other words, these x-ray methods showed that a time interval was required to build up the fiber structure. This result was consistent with the longer time required at 380 per cent elongation.

It remained to determine roughly the curve representing the rate at which the fiber structure was built up under these experimental conditions—namely, a cyclic stretch of 420 per cent attained in 0.6 second. This was done by setting the commutator connections ( $O$  of Figure 1) to open the shutter for approximately 1.5 seconds during each cycle, and by predetermining the time interval between the completion of the cyclic stretching and the opening of the shutter (Figure 2c). The total time of actual exposure of all the photographic films was kept at 1 hour and 45 minutes, so that the original negatives could be compared to show the relative intensities of the fiber patterns. Figure 3 is a schematic diagram showing the growth of the fibrous condition in the rubber with the duration of stretch.

There are at least four obvious explanations for the experimental facts of Figure 3. One of these has already been given—namely, that time is required for the transfer of unfavorably oriented molecules out to the boundaries of fibers made up of favorably oriented molecules. It hardly alters the mechanics of this simple picture to assume molecular chains which are twisted like a tangle of twine. Such a modified picture merely substitutes portions of the molecule which is being stretched, for separate molecules which have to be squeezed out of the way. A second possible explanation would be that the time lag is inherent in the process of producing an orientation in those molecules which have become stretched. The first explanation assumes molecules whose ends are aligned in the direction of stretch, but whose middles are pushed out of line so that true orientation requires time. The second explanation assumes molecules whose ends are not aligned in the direction of stretch and assumes that after a time interval the ends, along with the rest of the molecule, succeed in pushing away any conflicting molecules, thus giving a perfect alignment. The authors find this explanation hard to accept because the nearer they are to perfect alignment, the less are the forces tending to produce further alignment of the ends. Because of the length of the molecules, these forces should be much smaller than the forces in the first case. Although the authors do not assign any high degree of probability to the correctness of this second explanation, still it cannot definitely be thrown out. It seems preferable in-

stead to regard it as a variant of the first of the proposed explanations. A third explanation would be that the time lag is inherent in the mechanics of stretching the favorably oriented molecules themselves. So far, such an explanation offers considerable difficulty to the authors, partly because it seems hard to picture the mechanism of a time lag in stretching a simple spiral, and partly because such a picture does not lend itself to the real purpose of a theory; that is, it does not suggest new data and new lines of attack. The fourth explanation is that fibering is delayed merely because of the temporary temperature rise which accompanies the stretching of rubber. The amount of experimental work necessary to confirm or dispose of this explanation is very great, and it will be some time before it can be completed. There are, however, data which make an explanation based on temperature seem highly improbable. Using a thermocouple of fine wire (B. S. No. 30) with a very fine junction imbedded in the rubber strip, it was not found possible to demonstrate experimentally

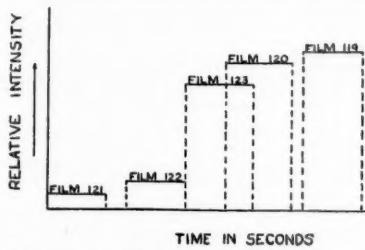


FIGURE 3. GROWTH OF FIBER STRUCTURE

a temperature rise of more than  $1^{\circ}\text{C}$ . even when the rubber was stretched 480 per cent. (This stretch is to be compared with a stretch of 420 per cent in the x-ray experiments.) An equal drop in temperature was measured upon relaxing the rubber strip. Additional evidence against any explanation based on temperature is found in a calculation of the maximum possible rise in temperature due to stretching. A force-elongation curve was plotted for the rubber strip under investigation, using short-time forces. The work of stretching 420 per cent was found graphically. This work was expressed in calories. By the aid of the specific heat of rubber (I. C. T. data) and the mass of the rubber strip, the temperature was calculated which the rubber would have attained if all the mechanical work had been converted into heat and if there had been no heat losses from the surface. This gave a maximum possible temperature rise of  $5.2^{\circ}\text{C}$ . It is hard to believe that such a small temperature rise could seriously reduce the intensity of the diffracted beams of x-rays.

#### ACKNOWLEDGMENT

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RECEIVED June 2, 1931. The combined material of two papers on "An X-Ray Method of Studying the Nature of Gels," and "X-Ray Evidence that Rubber Is a Two-Phase System," presented before the Divisions of Colloid and Rubber Chemistry, respectively, at the 82nd Meeting of the American Chemical Society, Buffalo, N. Y., August 31 to September 4, 1931. Largely based on a thesis submitted by M. F. Acken in partial fulfilment of the requirements for the degree of doctor of philosophy at Pennsylvania State College.

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## Reactions during Vulcanization

### I—Influence of Zinc and Lead on Rate of Cure of Stocks Accelerated with Tetramethylthiuram Monosulfide<sup>1</sup>

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The acceleration of the vulcanization of rubber by thiurams at low temperatures is reduced by the addition of free lead oxide and water-soluble lead salts, but not by insoluble lead salts. The retardation is due to the inactivation of part of the accelerator by the lead through the formation of an insoluble compound, and the amount inactivated is related to the amount of lead present. An equilibrium apparently exists between the amounts of zinc oxide and lead oxide and the accelerator, which is ordinarily on the side of a very large amount of the lead compound.

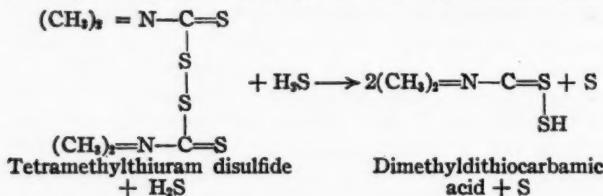
When an excess of the thiuram is present, a white product can be obtained even when litharge is present in the stock, which indicates further that the lead combines with the accelerator to form an insoluble material inactive at low temperatures. The increasing activity of the lead compound with increasing temperatures can be explained by increasing solubility in rubber. The insolubility of the lead compound is further indicated by the fact that if the thiuram is added to a stock containing soluble lead, it is less effective than if it had been added after the lead so that the particles of accelerator would have had time to disperse in the rubber, rather than be coated by the insoluble lead compound.

Since large amounts of accelerator are required to obtain an equivalent state of cure when lead is present, considerable hydrogen sulfide is required to convert the

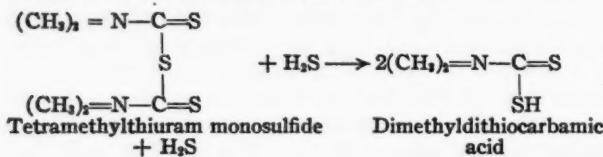
<sup>1</sup> Received September 10, 1931. Presented before the Division of Rubber Chemistry at the 82nd Meeting of the American Chemical Society Buffalo, N. Y., August 31 to September 4, 1931.

thiuram to the dithiocarbamate, and accordingly the initial set-up cure is delayed. A considerable delay in set-up can be obtained also by increasing the amount of fatty acid, and thus the amount of zinc soaps which will remove hydrogen sulfide as fast as it is formed.

**A** MECHANISM of vulcanization reactions with tetramethylthiuram disulfide has been suggested by Bedford and Sebrell (1). They present evidence to show that hydrogen sulfide, which is formed during vulcanization by the action of sulfur on the non-rubber constituents of crude rubber, reacts with tetramethylthiuram disulfide and zinc oxide to form zinc dimethyldithiocarbamate. The reaction proceeds further in the presence of more hydrogen sulfide liberating dimethylamine and carbon disulfide, which on coming in contact with a zinc oxide particle, reform zinc dimethyldithiocarbamate. As evidence of this mechanism, these investigators (1) have demonstrated that a cement containing large amounts of tetramethylthiuram disulfide, sulfur, and zinc oxide will vulcanize on standing at ordinary temperatures if treated with a small amount of hydrogen sulfide, because of the action of zinc dimethyldithiocarbamate



which is formed in the presence of zinc oxide, and which accelerates vulcanization at low temperature. In the course of the present investigation, it has been found that under favorable circumstances cements of tetramethylthiuram monosulfide will also vulcanize upon treatment with hydrogen sulfide, which indicates that both the thiuram mono- and disulfides form the same active material.



The difference between the two reactions is that the second sulfur atom in the disulfide is available for vulcanization, whereas the monosulfide will vulcanize rubber only after sulfur has been added.

The rapid cure with the zinc salt of dimethyldithiocarbamic acid at low temperatures (115° C.) is illustrated in Figure 1, together with the slow cure of the lead salt. The similarity in the effect of small amounts of soluble lead compounds (the sulfate being insoluble and therefore inert) on the rate of

cure of twenty-volume zinc oxide stocks compounded with tetramethylthiuram monosulfide and tetramethylthiuram disulfide further points to a common mechanism in the action of the two accelerators (Figures 2 and 3).

It is generally recognized that zinc and lead oxides react with the organic acids present in rubber and that the soluble soaps in turn react with accelerators. Figure 1 shows that although lead dithiocarbamate cures slowly at low temperatures, it is nearly as fast as the zinc compound at high temperatures, and the data assembled in this paper have led to the conclusion that the differences in behavior of the two compounds are due to differences in solubility of reaction products of the two accelerators in the rubber-sulfur mixture.

#### Translucency and Opacity of Stocks

In order to obtain direct evidence, compounds containing 2 per cent of accelerator with and without sulfur were placed between glass plates and cured at 115° and 150° C., and the appearance was noted as follows:

	ZINC DIMETHYL-DITHIOCARBAMATE	LEAD DIMETHYL-DITHIOCARBAMATE
Rubber-sulfur at 115° C.	Translucent	Opaque
Rubber at 115° C.	Opaque	Opaque
Rubber-sulfur at 150° C.	Translucent	Translucent <sup>a</sup>
Rubber at 150° C.	Opaque	Opaque

<sup>a</sup> Very dark due to precipitated lead sulfide.

#### Effect of Increasing Amounts of Accelerator

In accordance with the general chemical principle that when a substance is in a position to react with two other materials the reaction will proceed most completely in the direction to form the more insoluble compound, it follows that when dimethyldithiocarbamic acid is free to react with zinc oxide and lead oxide at 115° C., the lead compound should be formed almost to the exclusion of the zinc compound. The facts confirming the prediction of the formation of the lead salt are illustrated in Figure 4, where tests on a twenty-volume leaded zinc oxide stock are shown.

*Note*—With the exception of three curves in Figure 9, the samples of zinc oxide used were Red and Black Label Kadox which have a particle size of about 0.15 micron, the Red Label sample containing 0.87 per cent of free lead oxide and the Black Label 0.10 per cent. In this paper Red Label Kadox is referred to as leaded zinc oxide and Black Label as a low-lead zinc oxide.

The addition of 0.5 to 1.5 per cent tetramethylthiuram monosulfide calculated on the rubber developed slow rates of cure, all similar and indicating a lead dithiocarbamate or litharge cure. When the tetramethylthiuram monosulfide content was increased by another 0.5 to 2 per cent, the compound yielded a fast cure indicative of zinc dimethyldithiocarbamate acceleration. The equilibrium is apparently displaced in the direction of the lead compound—that is, the insoluble lead accelerator is formed in preference to the zinc accelerator, and the resulting cure is due to litharge until enough acceler-

ator has been added to combine with practically all the lead, when the additional accelerator will form the zinc salt.

On a stoichiometric basis using the equations as shown, a typical zinc accelerator cure should be obtained with above 1 per cent of accelerator (Figure 4), whereas more than 1.5 per cent of accelerator was required. The larger amount of

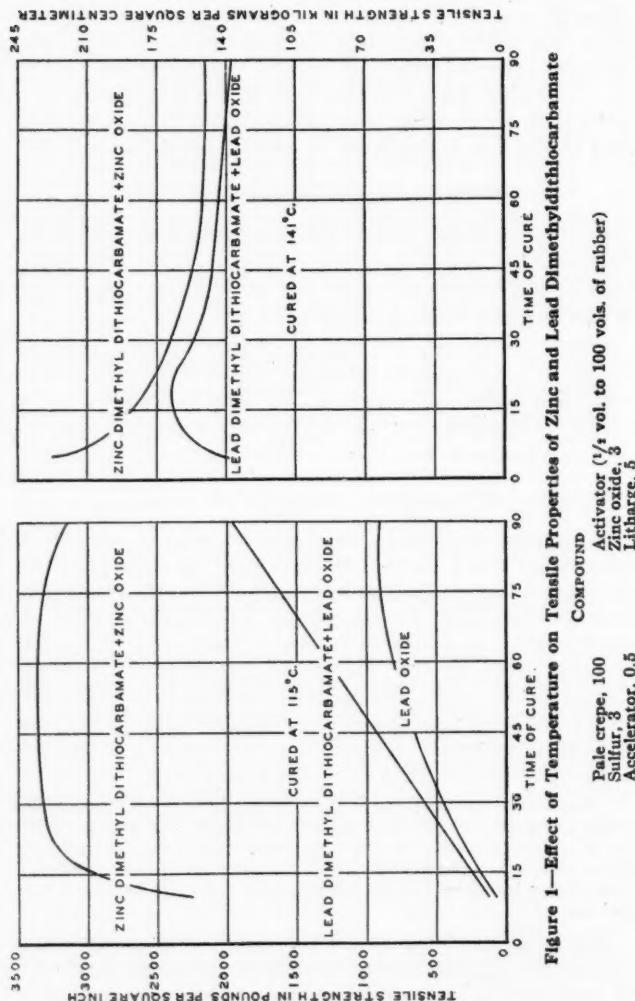


Figure 1—Effect of Temperature on Tensile Properties of Zinc and Lead Dimethylthiocarbamate Compound

Pale crepe, 100  
Activator ( $\frac{1}{4}$  vol. to 100 vols. of rubber)  
Zinc oxide,  $\frac{3}{8}$   
Sulfur,  $\frac{3}{8}$   
Accelerator, 0.5  
Litharge, 5

accelerator needed is probably owing to the formation of 30 to 50 per cent of inactive tetramethylthiourea through a side reaction, as suggested by Maximoff (9).

Now consider the color changes in these stocks (Figure 5); the lead, in excess of that which goes to form the lead accelerator, reacts with hydrogen sulfide generated during vul-

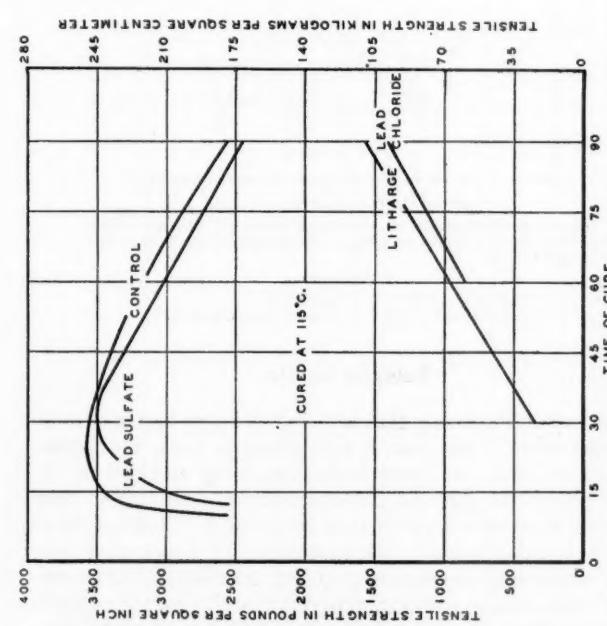


Figure 2—Influence of Lead Compounds on Rate of Vulcanization with Tetramethylthiuram Monosulfide  
 COMPOUND  
 Rubber, 100  
 Sulfur, 3  
 Low-lead zinc oxide, 122  
 Impurity, 6  
 Accelerator, 0.6

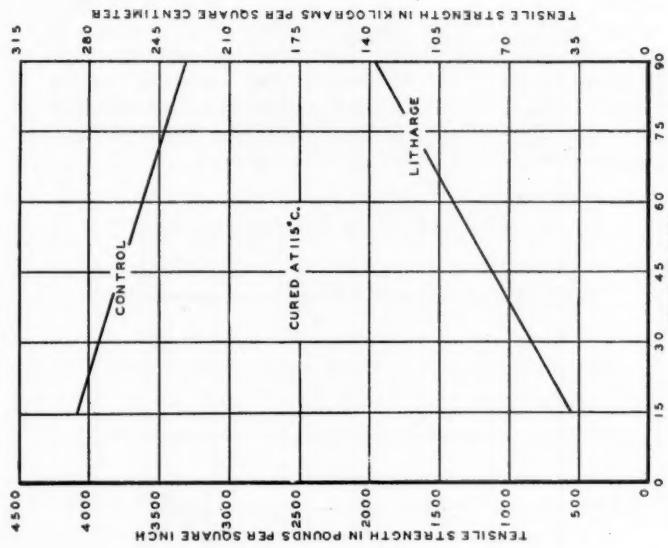


Figure 3—Influence of Lead Oxide on Rate of Vulcanization with Tetramethylthiuram Disulfide (Same Type Formula as in Figure 2)

canization and appears as black lead sulfide. It should be noted that the discoloration decreases with increase of accelerator content, since more of the lead is retained as light-colored lead dimethyldithiocarbamate. Finally, when all of the available lead oxide is combined as lead dimethyldithiocarbamate (2 per cent accelerator calculated on the rubber), a white stock is obtained and the surplus accelerator reacts with the zinc oxide to form soluble zinc dimethyldithiocarbamate, resulting in a well-cured compound.

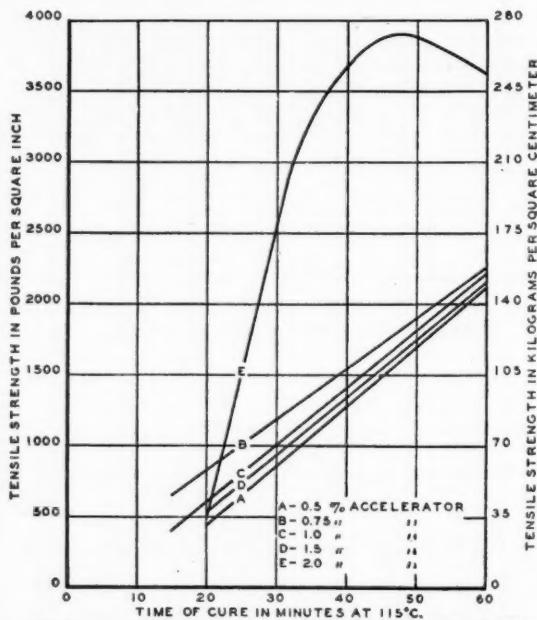


Figure 4—Influence of Concentration of Tetramethylthiuram Monosulfide on Stock Containing Small Amount of Lead Oxide

COMPOND  
Pale crepe, 100      Sulfur, 3  
Accelerator, 0.5-2.0      Leaded zinc oxide, 122

#### Delayed Set-Up

It is rather surprising that although a much better cure is obtained when 2 per cent of accelerator is used, the initial cure comes later, an appreciable cure being attained in 15 minutes with 0.5 per cent of accelerator and no cure in this length of time with 2 per cent of accelerator. Bedford, in a private communication, has expressed the belief that the larger amount of accelerator required considerable amounts of hydrogen sulfide, forming relatively inactive lead dimethyldithiocarbamate, and that there was insufficient hydrogen sulfide for a time to form the active zinc dimethyldithiocarbamate.

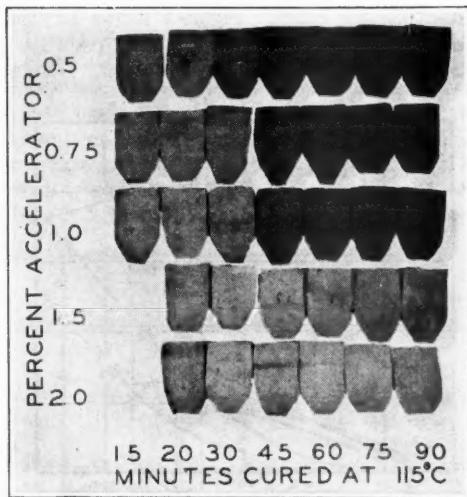


Figure 5—Influence of Concentration of Tetramethylthiuram Monosulfide on Color Changes of Stocks (Same Stock as in Figure 4)

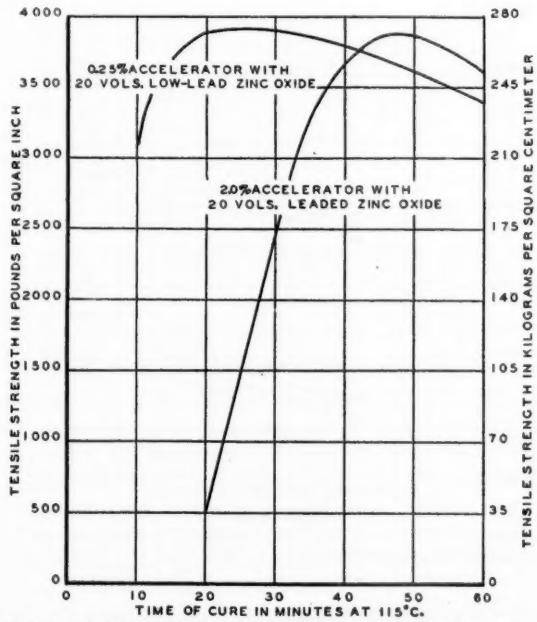


Figure 6—Comparison of Leaded with Low-Lead Zinc Oxide in Twenty-Volume Stocks

Delayed thiuram cures through the addition of lead oxide have been recommended to the rubber trade (2), and these data substantiate the claim. Figure 6 shows an example of the greater delayed cure for a leaded zinc oxide stock compared with that for a low-lead zinc oxide stock. This example

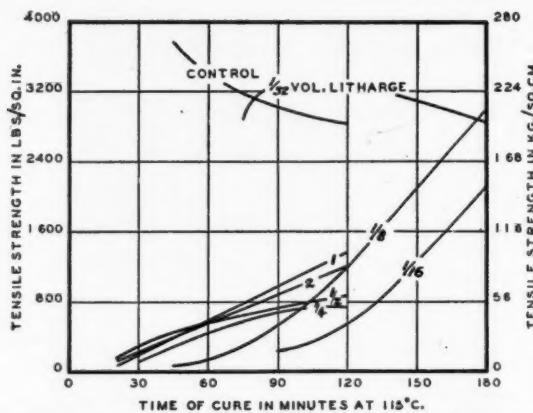


Figure 7—Effect of Lead Oxide on Vulcanization with Tetramethylthiuram Monosulfide

COMPOUND	
Rubber, 100	Low-lead zinc oxide, 6
Tetramethylthiuram monosulfide, 0.5	Litharge, 0-20
Sulfur, 3	

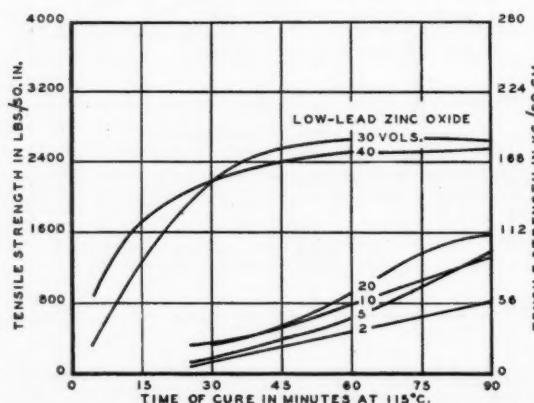


Figure 8—Effect of Mass Action in Litharge Stock by Increasing Zinc Oxide Content

COMPOUND	
Rubber, 100	Litharge, 2.5 ( $\frac{1}{4}$ volume)
Tetramethylthiuram monosulfide, 0.5	Low-lead zinc oxide, 12.2-24
Sulfur, 3	(2-40 volumes)

is not so convincing as it might be, since the rates of cure are different. Other tests have shown that this delayed cure persists, however, even when larger amounts of accelerator are used with the leaded oxide.

### Effect of Increasing Amounts of Litharge

It will be observed (Figure 4) that the amount of lead dithiocarbamate in the compound did not greatly alter the tensile properties, since the almost negligible solubility of lead dimethyldithiocarbamate in rubber at this temperature (115° C.) limited the activity of the accelerator. The quantities of lead oxide introduced in the compounds so far discussed have been small, consisting of the amount present in the zinc oxide. A series of tests with litharge added in amounts up to and above that necessary to combine with all the tetramethylthiuram monosulfide, shows that the excess

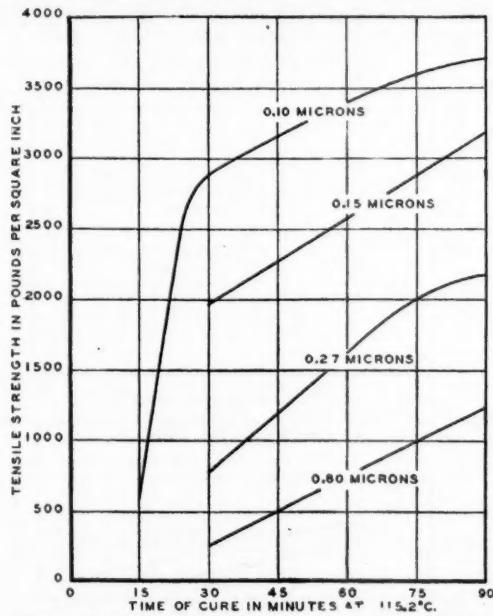


Figure 9—Influence of Particle Size of Zinc Oxide on Rate of Cure of Stock Containing Small Amount of Litharge

	COMPOUND	
Rubber, 100		Litharge, 2.5
Tetramethylthiuram monosulfide, 0.5		Zinc oxide, 122
Sulfur, 3		

(The fine and the coarse zinc oxides are experimental)

lead oxide develops a litharge cure (Figure 7). The cure is retarded at first with increasing amounts of litharge, owing to removal of the accelerator as an insoluble material, but with increasing amounts of litharge, the rate of cure increases slightly once more due to a litharge cure. The change when  $\frac{1}{8}$  of a volume of litharge is added is shown visually by a change in color; with less litharge the stock is light-colored and with more it is black.

## Equilibrium between Zinc and Lead Salts

The limited solubility of lead dimethyldithiocarbamate with the equilibrium so far on the side of the lead compound

and the development of a litharge cure with added amounts of litharge preclude the possibility of clearly showing the mass action phenomena with the group of compounds just men-

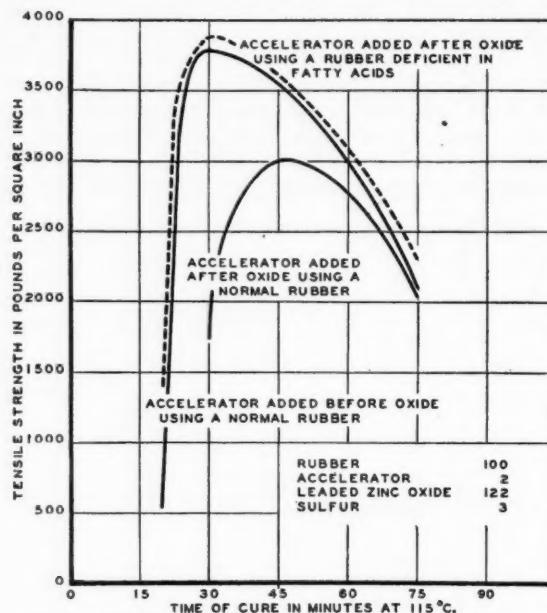


Figure 10—Effect of Order of Addition of Zinc Oxide and Accelerator during Cure—I

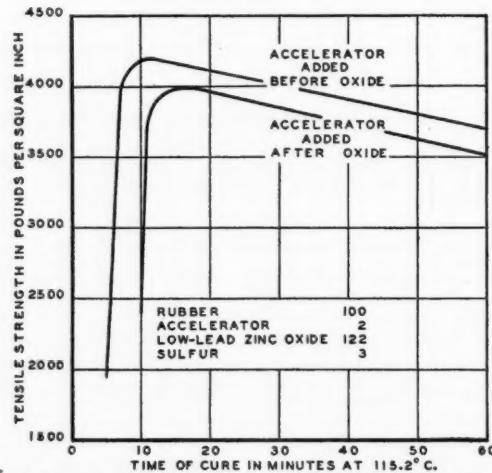


Figure 11—Effect of Order of Addition of Zinc Oxide and Accelerator during Cure—II

tioned. Driving the equilibrium reaction in the other direction by an increased concentration of zinc oxide, however, does not present such difficulties. Added amounts of

zinc oxide surface to a low-litharge compound increase the rate of cure and tensile properties of the compounds, as illustrated in Figure 8.

Presumably the accelerator, or more specifically the reaction product of the accelerator, dimethyldithiocarbamic acid or a polysulfide of it, is in equilibrium with zinc and lead as their corresponding dimethyldithiocarbamates. With increments of zinc oxide, the concentration of zinc dimethyldithiocarbamate is increased by mass action and the fast cure of the zinc derivative becomes effective, until in high-volume zinc oxide stocks (30 to 40 volumes) a large amount of the dimethyldithiocarbamic acid is present as the zinc salt, and ultimately tensile values are obtained which approach those of a stock containing only the zinc accelerator.

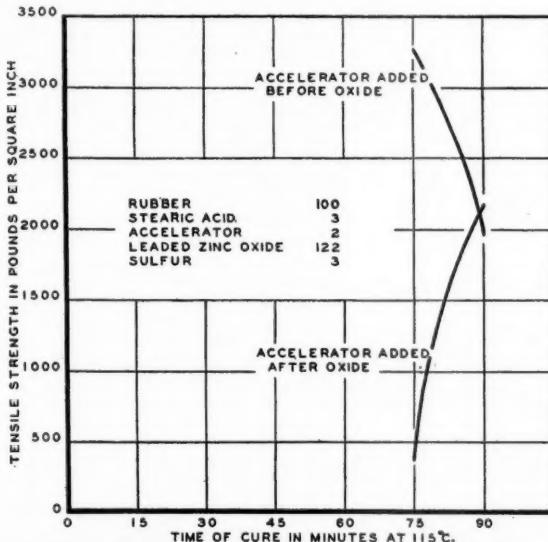


Figure 12—Influence of Stearic Acid on Mixing Order

The mass action mechanism whereby increments of zinc oxide in a low-litharge stock have increased the rate of cure with tetramethylthiuram monosulfide is also demonstrated in Figure 9, which shows that equal volumes of zinc oxides of increasingly fine particle size increase the rate of cure by virtue of the greater amount of zinc oxide surface available for influencing the equilibrium.

#### Order of Adding Ingredients

The data that have been shown were obtained on stocks in which the accelerator was milled in thoroughly before the addition of pigment. The zinc oxide was added after the accelerator, and the sulfur last. It was found necessary to standardize this procedure, especially for stocks containing free lead oxide, since the order of mixing makes a considerable

difference, as shown by the results in Figure 10. When the lead content was lowered, the order of mixing had less effect, as shown in Figure 11. In order to eliminate the mechanical effect of mixing on the dispersion of the accelerator, tests were made in which the time of mixing after the addition of the accelerator was the same, but this appeared to be a secondary consideration. Since the accelerator required only a fraction of a minute to add, the time that the accelerator and pigment were mixed together was also practically constant.

The explanation of the variability in rate of cure with different orders of adding the ingredients is the same as has been advanced throughout this paper—namely, the solubility of the lead compound of the accelerator. When lead oxide is mixed into rubber it reacts with the fatty acid present and forms lead soaps. These lead soaps migrate to particles of the thiram accelerator and react with them, forming insoluble coatings around the accelerator particles. When rubber deficient in fatty acid content is used instead of normal rubber, relatively less lead goes into solution and the accelerator disperses satisfactorily even when added after the oxide, giving a curing curve which compares favorably with the curve for the accelerator added first, using rubber, as shown in Figure 10.

#### Effect of Soaps on Set-Up Cure

The addition of stearic acid exaggerates the effect by enabling the formation of more soluble lead and thereby coating the thiram particles more thoroughly (Figure 12). The larger amount of soluble lead, when stearic acid is added, absorbs more hydrogen sulfide and thereby develops a delayed cure, but the order of adding the ingredients becomes increasingly important.

The large number of variables that affect the cure when the thiurams are used makes it more difficult to obtain laboratory check tests using these materials than with many other accelerators, and work that is done in this field must be carried out under carefully standardized conditions.

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# Oxidation Studies of Rubber, Gutta-Percha, and Balata Hydrocarbons<sup>1</sup>

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The oxidation mechanism of rubber and gutta-percha hydrocarbons has been studied. Rubber hydrocarbon in sheet form oxidizes more slowly and less completely than precipitated gutta-percha, which is believed to be due to the smaller surface exposure of the former material. Gutta-percha hydrocarbon in finely divided form oxidizes to a fairly definite degree in oxygen at room temperature, corresponding to a weight increase of about 38 per cent. The length of the autocatalytic induction periods for rubber and gutta-percha varies over a wide range and is shortened by heating the hydrocarbon in high vacuum before oxidation and by exposure to light.

The rate of oxidation of gutta-percha in air, as compared with oxygen, is reduced in proportion to the oxygen concentration, and the induction period is correspondingly increased.

Carbon dioxide, water, formic acid, and formaldehyde are identified in the volatile oxidation products, and their relative amounts determined. Six to eight per cent of the hydrocarbons are converted to volatile oxidation products. The percentage unsaturation of both rubber and gutta-percha hydrocarbons is reduced in proportion to oxygen absorbed. The ratio of hydrogen to carbon decreases as a result of oxidation.

The solid oxidized products are of such a nature that they cannot be resolved into crystalline materials. They are amorphous acid substances, free from aldehyde and ketone groups. They contain a small amount of peroxides; and the acidity, saponification value, and other properties indicate that most of the oxygen is combined in the form of hydroxyl, carboxyl, and lactonic groups. The mechanism of oxidation of rubber and gutta-percha appears to be the same, and the possibility of a chain mechanism to explain the facts is discussed.

<sup>1</sup> Received September 10, 1931. Presented before the Division of Rubber Chemistry at the 82nd Meeting of the American Chemical Society, Buffalo, N. Y., August 31 to September 4, 1931.

**T**HE chemical and physical changes taking place in rubber, gutta-percha, and balata as a result of oxidation have already been the object of many investigations. However, on account of the difficult nature of the subject progress has been slow, and there are many questions concerning the mechanism of the oxidation process as well as the constitution of the hydrocarbons which still remain to be answered.

In general, oxidation reactions are likely to be very complicated. For example, Lenher (16) has recently found that a simple material, such as ethylene, oxidizes to form dioxy-methyl peroxide, acetaldehyde, formic acid, the oxides of carbon, hydrogen, and water in a stepwise manner. As regards rubber and gutta-percha hydrocarbons, further complications are added by the fact that these materials have very complex and unknown structures.

The present paper gives an account of experiments carried out to determine more exactly the nature of the products resulting from the oxidation of rubber and gutta-percha hydrocarbons when exposed to oxygen for several weeks or months at ordinary temperatures.

#### Previous Work

Hofmann (13) noted that gutta-percha absorbs oxygen from the atmosphere and changes into a hard brittle material. Spiller (25) extracted a rubber-coated fabric, which had been exposed to air for 6 years, with alcohol and obtained a shellac-like substance (Spiller's resin), to which he assigned the formula  $C_{30}H_{48}O_{10}$ . Herbst (12) passed a current of air through a hot benzene solution of rubber for 140 hours and obtained a transparent reddish brown sirup, soluble in light petroleum and having a composition of  $C_{10}H_{16}O$ , and an insoluble residue which was an amorphous friable yellow solid of the composition  $C_{10}H_{16}O_3$ . Ramsay, Chick, and Collingridge (23) passed air through a toluene solution of gutta-percha for 14 days and obtained an acidic product completely soluble in alcohol and acetone, and having the empirical composition of  $C_{11}H_{18}O_3$ . Peachey (21) and later Peachey and Leon (22) exposed thin films of acetone-extracted crepe rubber and balata hydrocarbon to oxygen at  $85^\circ C.$ , finding that rubber absorbed approximately 4 atoms of oxygen per  $C_{10}H_{16}$ , while balata absorbed about 5 atoms. Large quantities of carbon dioxide were found in both cases. Dawson and Porritt (5) followed the gain in weight of balata hydrocarbon in a current of air at room temperature in diffused daylight. An S-shaped curve was obtained when they plotted oxygen absorption against time, showing the autocatalytic nature of the reaction. When the oxidized balata was suspended in water and treated with starch iodide solution, an appreciable amount of iodine was liberated, indicating the presence of peroxides which were believed to be the autocatalytic agents. An analysis of the product corresponded empirically to  $C_{10}H_{16}O_3$ . They were unable to detect any formation of carbon dioxide during oxidation, this variance

with Peachey and Leon's results being attributed to the fact that air at ordinary temperatures was used, while Peachey and Leon (22) employed oxygen at 85° C. They found about 0.3 per cent of formic acid given off by the balata during oxidation.

Mead and Pope (18) found that, when rubber oxidized at temperatures ranging from 30° to 100° C., various amounts of carbon dioxide and water were formed, depending on the temperature at which the oxidation took place.

Robertson and Mair (24) treated rubber, dissolved in chloroform, with aqueous solutions of potassium permanganate and obtained oxidation products which contained varying amounts of oxygen, depending on the ratio of permanganate to rubber used. These products differed from those obtained from the air oxidation in being insoluble in alcohol, acetone, and dilute alkalies. Formic, acetic, oxalic, and levulinic acids were detected in the aqueous phase. These same authors treated rubber, dissolved in chloroform, with hydrogen per-

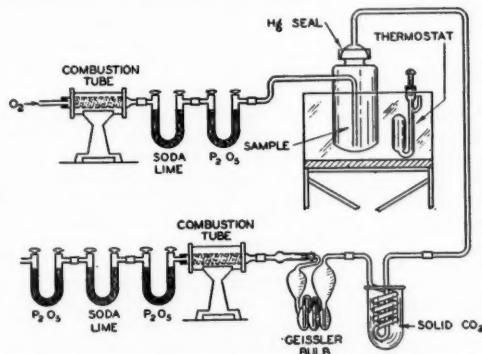


Figure 1—Apparatus for Collection of Volatile Oxidation Products

oxide in the presence of glacial acetic acid, and found 1 mole of carbon dioxide split off from a complex of 40 to 45 carbon atoms. The oxidized rubber in this case was found to be soluble in alcohol, acetone, and alkalies. With moderate amount of hydrogen peroxide it appeared that the oxygen combined as hydroxyl, whereas with larger quantities resin acids were formed.

#### Materials and Procedure

The materials used in this investigation were crude Surinam sheet balata, Pahang and Goolie Soondie gutta-percha, and the best grade pale crepe rubber.

The balata and gutta-percha samples were purified by dissolving 50 grams of crude material in 1600 cc. of chloroform. The insoluble matter was completely removed by repeatedly shaking the solution with distilled water, allowing it to stand each time for about 1 week in the dark before separating the two layers, the insoluble matter remaining in the aqueous layer. The chloroform solution was then filtered into five

or six times its volume of acetone. The hydrocarbon separated as a snow-white mass. After standing for several days, the acetone was poured off and the precipitate redissolved in chloroform. The solution was again filtered and reprecipitated by allowing it to slowly run into five or six times its volume of absolute alcohol. Several reprecipitations were generally practiced. Throughout all operations an atmosphere of carbon dioxide was maintained over the solutions. The hydrocarbon was finally dried in a current of pure nitrogen at 40° C. or in high vacuum at 50° C.

These samples were 98.5 to 99.7 per cent pure, as determined by combustion and unsaturation. They contained only minute amounts of ash or nitrogen. The principal impurity was oxygen, apparently contained in substances very difficult to remove, but not believed to be oxidation products. The hydrogen-carbon ratio was in every case close to 1.60. These results are in conformity with those of several other investigators (19) who have found it very difficult to remove the last traces of oxygen-containing impurities. Pure rubber hydrocarbon was prepared from acetone-extracted crepe, using diffusion methods similar to those employed by Caspary (4) and Feuchter (9). This material was ash-free and contained only traces of nitrogen and oxygen.

Samples of the finely precipitated gutta-percha and balata hydrocarbons were weighed into tared containers and placed in a vacuum-type desiccator exposed to diffused light in the laboratory. The opening in the lid was fitted with a rubber stopper containing an inlet tube, reaching to the bottom of the desiccator, and a short outlet tube. Dry oxygen at room temperature (20° to 30° C.) and at ordinary pressure was passed continuously through the system. The samples were removed periodically and weighed to determine their increase in weight. The rubber specimens in the form of sheets of about 1 mm. in thickness were subjected to the same treatment.

A special apparatus used for the study of volatile oxidation products is shown in Figure 1. Purified oxygen was slowly passed over the sample and the volatile oxidation products, which were liquid or solid at the temperature of solid carbon dioxide, were collected in the cooling coil and weighed. Carbon dioxide or other acidic volatile oxidation products, not collected in the cooling coil, were collected in a Geissler bulb, containing potash solution, and weighed. For the detection of other low-boiling volatile products, such as carbon monoxide, methane, etc., the residual gas was passed through a combustion tube, and the water and carbon dioxide determined.

Chemical examination of the oxidized products was made by a variety of procedures which will be described later.

### Experimental Results

**RATE OF OXIDATION**—The progress of oxidation of various rubber, gutta-percha, and balata preparations is shown in Figures 2, 3, and 4. In the case of rubber, oxidation in no case appeared to be complete. In the case of gutta-percha, the results show that oxidation reached a fairly definite end point corresponding to a weight gain of about 38 per cent. When air was used instead of oxygen, the rate of oxidation decreased

as would be expected. The decrease in weight after the peak had been reached appeared to be due to the continued loss of volatile matter from the oxidized product. A pronounced autocatalytic effect was shown by most of the rubber and gutta-percha samples. The effect of preheating rubber hydrocarbon at 80° C. and above was definitely to decrease or eliminate its induction period. Precipitated balata hydrocarbon showed a very short induction period, but Dawson and Porritt (5) found this period to be about 10 days when the oxidation was conducted in air at 20° to 30° C. Peachey and Leon (22) showed that balata and rubber hydrocarbons had no induction period when carrying out the oxidation in oxygen at 85° C.

The rubber and gutta-percha hydrocarbons changed to a deep amber color during oxidation. The surfaces of the pure rubber sheets became hard and glassy, while the center portion was soft and pasty, showing that the oxidation took place principally on the surface and indicating that the oxidized product was a very effective seal against oxygen diffusion.

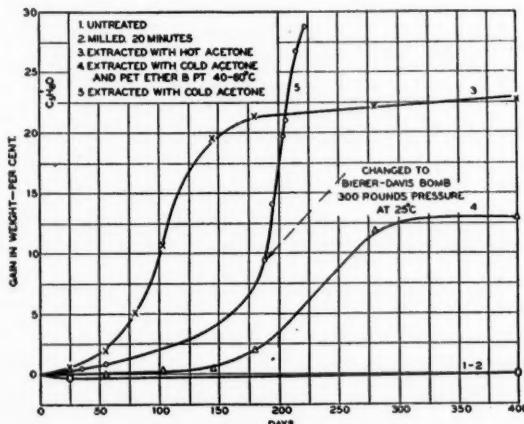


Figure 2—Rate of Oxidation of Crepe Rubber

Solid sheets of balata and gutta-percha hydrocarbons behaved in a similar manner. Acetone-extracted crepe rubber was found to be more suitable than the hydrocarbon for use in such oxidation studies on account of its tendency to oxidize to a higher degree. However, even with this material under the most drastic and prolonged treatment, there was evidence that oxidation was not complete, as the samples still continued to gain in weight after exposure to oxygen for 4 years.

**EFFECT OF LIGHT ON OXIDATION OF GUTTA-PERCHA—** Experiments were carried out by exposing gutta-percha hydrocarbon to oxygen at room temperature in the dark and also in diffused daylight in an effort to determine the effect of light on the rate of oxidation. As shown in Figure 5, the sample when stored in the dark had a longer induction period but otherwise absorbed oxygen in the same manner as the one placed in

diffused daylight. These results indicate that light does not radically affect the mechanism but reduces the induction period, and therefore accelerates the oxidation reaction. More extensive study is needed in this field, however, before definite conclusions can be drawn.

#### Volatile Oxidation Products

Acrid odors in the vapors arising from rubber and gutta-percha during oxidation were very pronounced. Qualitative tests of these vapors showed the presence of acids and aldehydes and traces of volatile peroxides, probably hydrogen peroxide. A more detailed study of these products was then carried out, using the apparatus shown in Figure 1. Purified

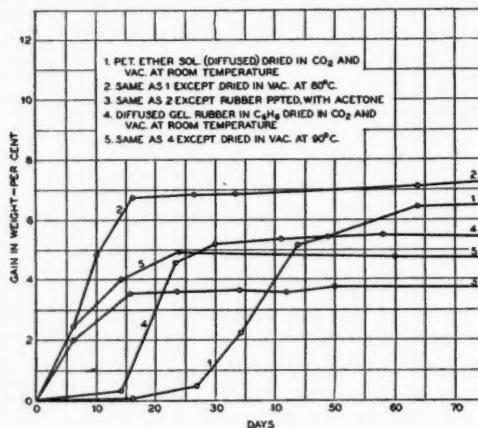


Figure 3—Rate of Oxidation of Rubber Hydrocarbon

oxygen was passed slowly over the sample kept at 25° C., and the volatile products given off were collected. A preliminary test was conducted on about 20 grams of balata hydrocarbon, in which the potash solution in the Geissler bulb was replaced with saturated barium hydroxide solution. A precipitate was formed in the baryta solution as soon as the oxidation had started, which increased in volume as oxidation proceeded. Analysis of this precipitate showed it to be barium carbonate. A yellow solid collected in the refrigerated coil, which melted between -10° to -14° C. and had a very pungent odor. A run with acetone-extracted crepe rubber gave similar results except that it took much longer to obtain an appreciable quantity of volatile matter. A quantitative study was then made, using 47.2 grams of balata hydrocarbon. The quantities of volatile materials collected are shown in Table I.

Table I—Quantity of Volatile Oxidation Products from Balata Hydrocarbon

	%
Gain in weight of sample	32.7
Gain in weight of cooling coil	2.56
Gain in weight of Geissler bulb (CO <sub>2</sub> )	2.90
H <sub>2</sub> O from combustion	0.23
CO <sub>2</sub> from combustion	0.66

The materials collected in the refrigerated coil gave strong positive tests for aldehyde with fuchsin solution and ammoniacal silver nitrate. Schryver's test indicated the presence of formaldehyde. Heating with caustic soda solution caused the formation of a brown insoluble resin, which also indicated the presence of aldehydes. The pyrrole test for levulinic aldehyde was negative. Large quantities of water were present.

A 15-cc. sample of the original liquid, obtained from the oxidation of 500 grams of balata hydrocarbon, was diluted to 110 cc., and 100 cc. was distilled in 10-cc. fractions; each was titrated according to the Duclaux (6) method. The remaining 10 cc. was titrated with standard potassium hydroxide to determine the original acidity. The Duclaux constants obtained by this distillation are shown in Table II, and they compare very closely with those for formic acid. These results also showed 21.8 per cent acid (calculated as formic) present in the original volatile liquid.

Further analysis of the volatile liquid included neutralization with barium hydroxide, followed by evaporation to dryness, and analysis of the residue after extracting it with ether. This analysis showed good agreement with barium formate. The ether solution was evaporated, and a red resinous material remained, which was not identified. From this examination it was concluded that the volatile liquid contained 21.8 per cent formic acid, 67.3 per cent water, and 10.9 per cent formaldehyde and other substances which were not identified.

Table II—Comparison of Volatile Liquid from Oxidation of Balata with Formic Acid by Duclaux Method

	A	B	C	D	E
Constants obtained	5.73	12.15	18.99	26.40	34.40
Duclaux constants for formic acid	6.04	12.66	19.66	27.35	35.51
Ratio obtained	1	2.1	3.3	4.6	6.0
Duclaux ratio	1	2.1	3.3	4.5	5.9

Table III gives results showing the relative quantities of volatile constituents given off during the oxidation of balata hydrocarbon, until it had gained 32.7 per cent in weight.

Table III—Volatile Oxidation Products from Balata Hydrocarbon

VOLATILE CONSTITUENT	QUANTITY COLLECTED:	
	On balata	On volatile
Carbon dioxide	2.91	51.4
Water	1.73	30.6
Formic acid	0.56	9.9
Formaldehyde and resinous matter	0.26	4.6
C + H in unabsorbed volatile products	0.20	3.5
Total	5.66	100.0

A run was made, using about 50 grams of acetone-extracted crepe rubber and the results showed the same volatile oxidation products present. Their relative amounts agreed quite closely with those for balata. The oxidation in this case was continued for 190 days, at the end of which time the weight gain was only 9 per cent. The total quantity of volatile oxidation products was therefore much less than in the previous run with balata.

Combustion analyses of highly oxidized rubber and gutta-percha have always shown a hydrogen-carbon ratio of less than 1.60. For example, the average value for completely oxidized gutta-percha is about 1.55. As carbon dioxide, water, formic acid, and formaldehyde are the principal volatile oxidation products in the proportion as shown in Table III, their hydrogen-carbon ratio, taken as a whole, is about 3. In other words, these results indicate that about 3 hydrogen atoms to 1 carbon are oxidized off the hydrocarbon in forming the volatile products, which accords with the lowering of the carbon-hydrogen ratio in the residual oxidized products.

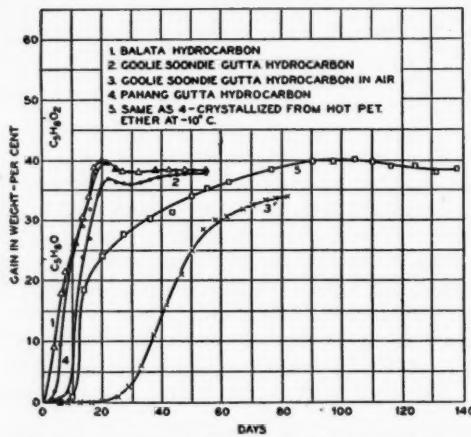


Figure 4—Rate of Oxidation of Gutta-Percha Hydrocarbon

Rubber and gutta-percha, after complete oxidation with elimination of volatile matter, show a weight gain of 6 to 8 per cent less than accords with the oxygen content of the oxidation products. This is accounted for by the loss of carbon and hydrogen in volatile oxidation products. The calculated amount of carbon and hydrogen in volatile matter given off as a result of oxidation of 1 gram of hydrocarbon is given in Table IV for rubber, gutta-percha, and balata.

Table IV—Amount of Volatile Oxidation Products Formed as Calculated from Weight Gain and Oxygen Content

	C + H IN ORIGINAL MATERIAL	WEIGHT GAIN	CARBON OXIDIZED MATERIAL	CALCULATED C + H IN VOLATILE		
				%	%	%
Crepe rubber <sup>a</sup> (acetone ext.).....	98.8	29.5	62.98			
Gutta percha (Pahang).....	98.5	38.4	57.90			
Gutta percha (balata).....	98.5	38.4	58.5			
HYDROGEN OXIDIZED MATERIAL			OXYGEN BY DIFFERENCE	MATTER FROM 1 GRAM	HYDROCARBON	
%.....			%.....	%.....	Gram	
Crepe rubber <sup>a</sup> (acetone ext.)....	8.36		28.66		0.064	
Gutta percha (Pahang).....	7.31		34.79		0.082	
Gutta percha (balata).....	7.63		33.87		0.070	

\* Heated to 70° C. before analysis.

These results indicate that the equivalent of two methyl groups are oxidized off from six to eight isoprene units, forming carbon dioxide, water, formic acid, and formaldehyde in about the relative proportions found. Peachey and Leon (22) found more than 20 per cent carbon dioxide formed during oxidation of balata hydrocarbon in oxygen at 85° C. They failed to detect other volatile products, but this is readily explained, as moist oxygen was used, and formic acid would be absorbed by the potassium hydroxide used to estimate the carbon dioxide. Dawson and Porritt (5), on the other hand, detected traces of formic acid but failed to find carbon dioxide given off by balata hydrocarbon exposed to air at ordinary temperatures. As these authors led the vapors directly into barium hydroxide solution, the possibility exists that any barium carbonate formed might have been dissolved by the relatively large quantity of formic acid present.

To obtain more information on this point, a sample of balata was oxidized by substituting air for oxygen and using the same apparatus and methods for collection of volatile products as has been previously described. In this case barium hydroxide solution was substituted for potassium hydroxide solution. After 2 days a precipitate began to form in the barium hydroxide solution, which steadily increased in volume as oxidation proceeded. At the end of the run this precipitate was tested and found to be barium carbonate. The cooling coil also contained the same yellow solid as was previously collected during oxidation in pure oxygen. These results are to be expected, as there is no valid reason for the mechanism of oxidation to be different in air and oxygen.

#### Solid Oxidation Products

The highly oxidized products are hard brittle resins. They contain small amounts of peroxides and are strongly acidic. They are also readily saponified. When heated, they begin to soften at about 65° C. and melt at 85° to 90° C. Decomposition starts at 100° C.

The physical properties of rubber and gutta-percha hydrocarbons change progressively with oxidation. Both materials show an extensive loss of strength after a weight gain of only a few tenths of 1 per cent. In this respect their mechanical properties appear to be just as sensitive to oxidation as those of vulcanized rubber which, according to Marzetti (17) and Kohman (15) is mechanically deteriorated by about 1 per cent oxygen combining with it.

Solubility of the oxidized products in acetone, alcohol, glacial acetic acid, and caustic alkali increases progressively, while their solubility in ether, carbon disulfide, and hydrocarbon solvents progressively decreases with oxidation. Both rubber and gutta-percha remain completely soluble in chloroform throughout the oxidation process. Both hydrocarbons

are insoluble in carbon tetrachloride after oxidation, which result was not to be expected considering the close relationship of chloroform and carbon tetrachloride.

The oxidized materials, like most other reaction products of rubber and gutta-percha, are amorphous and cannot be changed to a crystalline state, although many attempts were made in this direction.

Long boiling with Fehling solution and alkaline silver nitrate shows only slight reduction. Attempts to form crystalline derivatives from oxidized gutta-percha by treatment with phenyl hydrazine, hydroxylamine, acetyl chloride, acetic anhydride, dimethyl sulfate, bromine, and various reducing agents were all unsuccessful. The oxidized hydrocarbons are therefore distinctly different from the corresponding ozonides which Harries (10) showed readily yield levulinic aldehyde almost quantitatively upon hydrolysis.

**CHANGE IN UNSATURATION WITH OXIDATION**—The unsaturation also decreases progressively but does not appear to be completely eliminated as a result of oxidation. The change in unsaturation during the course of oxidation of a sample of gutta-percha was determined by the Kemp (14) modified Wijs method, using chloroform in place of carbon disulfide as a solvent. These results, which are shown in Figure 6, indicate that the oxidation reaction proceeds by a uniform mechanism. Table V gives the values for unsaturation found for rubber and gutta-percha oxidized to the same degree, and for gutta-percha when completely oxidized. These results show that some unsaturation remains after complete oxidation of gutta-percha, and that rubber and gutta-percha have the same unsaturation when oxidized to the same degree as measured by weight gain; this indicates that the mechanism of oxidation of both hydrocarbons is the same.

Table V—Unsaturation of Highly Oxidized Rubber and Gutta-Percha

ACETONE-EXTRACTED CREPE RUBBER		GUTTA-PERCHA HYDROCARBON		BALATA HYDROCARBON	
Weight gain	Unsatura- tion	Weight gain	Unsatura- tion	Weight gain	Unsatura- tion
29.5	41.8	28.2	42.6	....	....
....	....	30.3	38.9	38.4	21.5
		38.4	22.0		

**EFFECT OF HEATING**—Completely oxidized gutta-percha was found to lose 6.7 per cent as a result of heating *in vacuo* for 1 hour at 100° C. Ten grams were heated gradually up to 200° C. in a current of pure nitrogen, and the volatile materials collected in a manner similar to that used for volatile oxidation products. The loss in weight of the sample was 12.9 per cent. The cooling coil retained 0.71 gram of a yellow-colored aqueous solution, freezing at -12° to -15° C. and containing acids and aldehydes. Seventeen-hundredths gram of carbon dioxide was collected. These products appear to be the same as the volatile products resulting from oxidation. However, the ratio of water to carbon dioxide is larger. The residual product is a hard brittle dark-red resin. Its composition, in

comparison with the original oxidized product, is shown by the following analysis, showing that more hydrogen than carbon is split off:

	OXIDIZED MATERIAL <sup>a</sup>	OXIDIZED MATERIAL <sup>b</sup>
Carbon	57.93	63.03
Hydrogen	7.31	7.19
Oxygen	34.76	29.78
Ratio H/C	1.51	1.36

<sup>a</sup> Weight gain, 38.4 per cent.

<sup>b</sup> Heated to 200° C. in nitrogen.

Using carbon dioxide in place of nitrogen, a run was made, and gaseous products unabsorbed by potassium hydroxide were found given off. This explains the difference in loss in weight of the sample and the weight of the volatile materials collected in the case where nitrogen was used. Ramsay (29) and co-workers, upon distilling highly oxidized gutta-percha *in vacuo*, obtained a yellow aqueous distillate and detected carbon monoxide, carbon dioxide, and methane in the vapors given off.

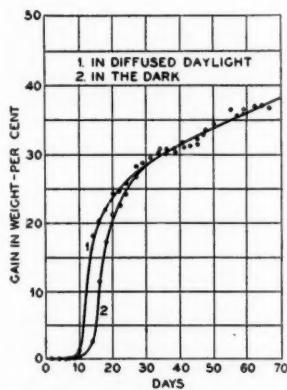


Figure 5—Effect of Light on Absorption of Oxygen by Pahang Gutta-Percha Hydrocarbon at Room Temperature

ACIDITY—The acid number and neutralization equivalents of highly oxidized rubber and gutta-percha were determined by titrating samples dissolved in alcohol with caustic, using phenolphthalein as an indicator:

	ACID NO.	NEUTRALIZATION EQUIVALENTS
Oxidized crepe rubber (weight gain, 29.5%)	91	620
Oxidized balata (weight gain, 38.4%)	83	680

SAPONIFICATION—Oxidized gutta-percha gave a saponification number of 254 as a result of boiling with an excess of aqueous normal alkali. Only traces of volatile acids, but no volatile alcohols, were detected in the saponification products. About 20 per cent of water-soluble resin acids were found, containing 54.08 per cent carbon, 6.88 per cent hydrogen, and 39.04 per cent oxygen. The water-insoluble acids were similar

in nature to the original material and had the following composition: carbon, 63.90 per cent; hydrogen, 7.59 per cent; and oxygen, 28.51 per cent. Saponification of 1 gram of the material in the presence of 125 cc. of normal sodium hydroxide and of 10 cc. of hydrogen peroxide gave a saponification value of 540. The products separated from this solution were also of a resin acid nature. These results indicate that additional carboxyl groupings are formed as a result of boiling with excess alkali, and that further oxidation of certain groupings to carboxyl result from the action of hydrogen peroxide. When hydrogen peroxide was added to an ammoniacal solution of the oxidized material, a white amorphous precipitate formed. This material, upon washing and drying, was found to be highly explosive and is probably a peroxide or superoxide. Attempts to crystallize it were unsuccessful.

**PEROXIDES**—Peroxides were detected in the oxidized material during the early stages of oxidation. The peroxide content of highly oxidized samples was determined as follows:

One-gram samples were dissolved in 25 cc. of glacial acetic acid, and 25 cc. of 15 per cent potassium iodide solution added. After standing 40 hours in the dark, the liberated iodine was titrated with 0.1 *N*  $\text{Na}_2\text{S}_2\text{O}_8$ , using starch indicator. A blank was also run at the same time.

SUBSTANCE	PEROXIDE OXYGEN	
	%	
Oxidized crepe rubber	0.48	
Oxidized crepe rubber (heated to 70° C.)	0.18	
Oxidized gutta-percha (balata)	1.9	
Oxidized gutta-percha (Pahang)	1.6	
Oxidized gutta-percha (Soondie)	1.8	

**MOLECULAR WEIGHT**—The mean molecular weight of oxidized gutta-percha was determined cryoscopically, using various solvents with the following results:

SOLVENT	MOLECULAR WEIGHT
Camphor	398
Menthol	403
Glacial acetic acid	216

These results, which at best are only indicative, show that oxidation breaks down the hydrocarbon complex into simpler units. Ramsay (23) obtained a value of 413 for the molecular weight of highly oxidized gutta-percha.

#### Discussion

The negative tests for aldehydes and ketones, the loss of moisture on heating, the acidity, the ease of saponification, the oxygen content, and the resin acid nature of the saponification products lead to the conclusion that the oxidized hydrocarbons are complex mixtures of hydroxy acids and lactones. It is of interest in this connection to note that Wallach (27) obtained a hydroxy acid and a lactone as a result of oxidizing alpha terpineol. Abietic acid oxidizes in air and changes to an alcohol-soluble material which cannot be

crystallized. It loses water upon heating and is believed by Henriques (11) to be lactonic, but Dupont and Dubourg (?) believe it to be a hydroxy acid.

Many previous investigators have ascribed molecular formulas to oxidized rubber, showing carbon and hydrogen atoms in proportion of 10 to 16 or a multiple thereof. These formulas are misleading, as non-homogeneity of the oxidized products together with the fact that the carbon and hydrogen ratio changes, owing to the splitting off of volatile matter, makes all of these formulas untenable.

Some investigators have also assumed that oxidation products of rubber and gutta-percha hydrocarbons are closely related to the resinous components in the natural gums. The only connection between these materials is that they contain oxygen and dissolve more or less completely in acetone. The resins of gutta-percha, balata, and rubber consist principally of sterol esters and are therefore chemically entirely different from the oxidation products.

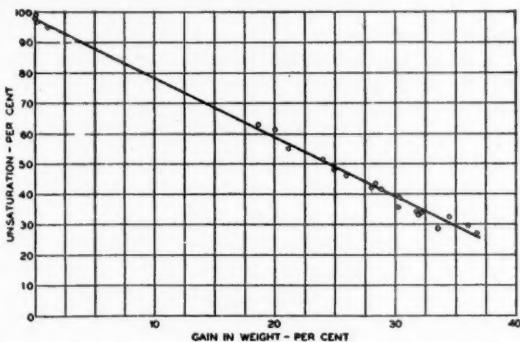


Figure 6—Effect of Oxidation of Gutta-Percha Hydrocarbon on Per Cent Unsaturation

Oxidation, like vulcanization, appears to produce changes in the rubber in proportion to the quantity of oxygen entering into reaction. However, it differs radically from vulcanization in being accompanied by much decomposition of the hydrocarbon.

So much evidence has accumulated that there is a fairly general agreement among investigators in this field that the first step in the oxidation reaction of rubber, gutta-percha, and drying oils, as well as many other unsaturated bodies, is a molecular addition of oxygen to the ethylene bond to form a peroxide.

The Bach-Engler (2, 8) theory of autoxidation considers an intermediate peroxide functioning as the catalyst. Moureu and Dufraisse (20) have amplified and extended this theory to explain the oxidation of many unsaturated substances, including rubber. Stephens (26), however, has recently pointed out that autoxidation can be explained if a chain type of reaction is assumed; this is favored because the chain type shows

a high degree of sensitivity to small amounts of inhibitors. Alyea and Böchstrom (1) have shown that inhibitors of oxidation are destroyed in the process of being oxidized. The intermediate peroxides may therefore act as catalysts by oxidizing the inhibitors.

Stephens also points out that, if autoxidations owe their induction periods to the presence of inhibitors, intensive purification ought to shorten and eventually eliminate this stage. He finds supporting evidence for this conclusion in the case of purifying cyclohexane. The present authors have also noted a striking case of this in connection with eleomargaric acid glyceride from tung oil, which, when highly purified, oxidizes with extreme rapidity in comparison with commercial tung oil and shows little or no induction period. Rubber hydrocarbon is another good example. One must keep in mind, however, that any preheating of a sample during purification may also affect the length of the induction period. This may be due to preoxidation if the heating is not conducted in the absolute absence of oxygen, which condition is very difficult to realize.

The authors believe that the induction period involves the building up of a peroxide concentration until the energy level reaches a point where the chain mechanism can operate. Inhibitors may function to reduce the energy level by reducing the peroxide, as most inhibitors are readily oxidized by peroxides. The oxidation of rubber and gutta-percha is quickly initiated upon exposure to light, which is in line with the already-known relation of photochemistry to chain reactions.

It has been noted that gutta-percha hydrocarbon generally begins to rapidly oxidize and turn yellow at spots, which is also an argument for the chain-mechanism theory, as it is well known that contact surfaces, which in this case may be foreign particles, may have a profound influence on oxidation reactions.

If a straight-chain structure of rubber is assumed the splitting of a methyl or methylene group to yield formic acid, formaldehyde, carbon dioxide, and water as accompanying reactions is a possibility. The oxidation of terpene hydrocarbons (3, 28) are good examples of this change where peroxide forms, followed by the splitting of the methylene group to yield formic acid and formaldehyde.

The continued combination of oxygen to the hydrocarbons does not stop with simple addition, as the final oxygen content is nearly double that of a simple addition product. In this respect oxygen reacts entirely differently from ozone, which forms an addition product.

The results indicate that the oxidized material contains compounds with at least 10, but more likely as many as 20 carbon atoms. The complex nature of these materials and their great resistance to being broken down into simpler units have so far been insurmountable obstacles in the way of their positive identification.

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## Scorch Retarders and Scorch-Retarding Materials<sup>1</sup>

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The effect of several softeners upon retardation of scorch is shown. This effect is also obtained by using small amounts of some organic materials which might be classified as scorch retarders. The effect of some of these materials upon the temperature coefficient of scorch is found to be of different value at different temperature increments below that of the curing temperature, and it seems that the temperature coefficient of scorching decreases as the temperature is raised.

**A** CLASS of materials, known as scorch retarders, has been available for some time and has been the subject of investigation in various laboratories for a considerably longer time. The ideal material of this type is one which can be added to a rubber compound and render it decidedly less "scorchy" at milling and calendering temperatures, yet not interfere with the curing rate of the compound at its curing temperature. Such a material should have no effect upon color, should not be detrimental to the aging properties of rubber compounds, and should be practically odorless when used in rubber; and its activity should be such that it is necessary to use only a small amount of the retarder.

Practical experience has taught that certain softeners are of benefit when scorching trouble is encountered in the factory, but the usual conception is that such ingredients soften the compound; the fact that these materials possess a definite scorch-retarding effect has not been so widely taught. The use of a scorch retarder seems to be a comparatively new practice, (1, 3, 5), but, as will be shown later, the industry has been using compounds which function as such for years.

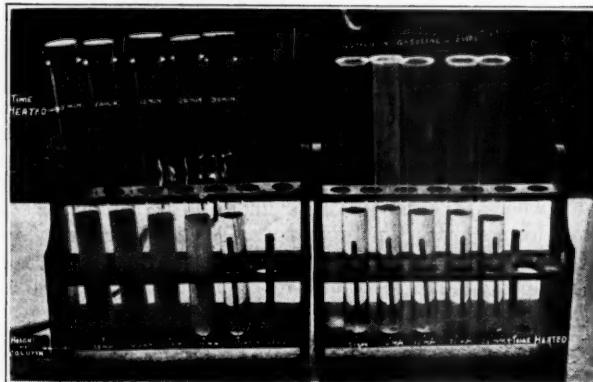
<sup>1</sup> Received September 10, 1931. Presented before the Division of Rubber Chemistry at the 82nd Meeting of the American Chemical Society Buffalo, N. Y., August 31 to September 4, 1931.

The effect that these materials have seems to indicate that the temperature coefficient at some temperature under that of the practical cure is altered by the scorch-retarding compound. If the same degree of cure is to be maintained in the same time in the presence of a scorch-retarding material as in its absence, and if at lower temperatures the material does hold off premature vulcanization, this change in temperature coefficient should be observable. In order to ascertain whether or not this condition is true, and in order to demonstrate the behavior of these retarding materials at various temperatures, the work reported herein was undertaken.

#### Method of Determining Scorch

The solubility method of determining scorch (6) was employed upon a compound of simple constituents. The compound consisted of the following ingredients:

Time heated (min.)	Soaked in gasoline
5	2 hours
10	
15	
20	
30	



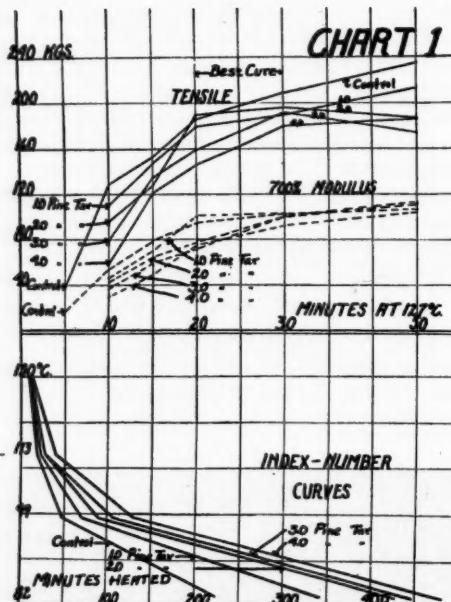
35 40 45 105 Clear  
Height of column (mm.)      5 10 15 20 25  
Time heated (min.)

Figure 1—Solubility and Swelling Tests on Rubber

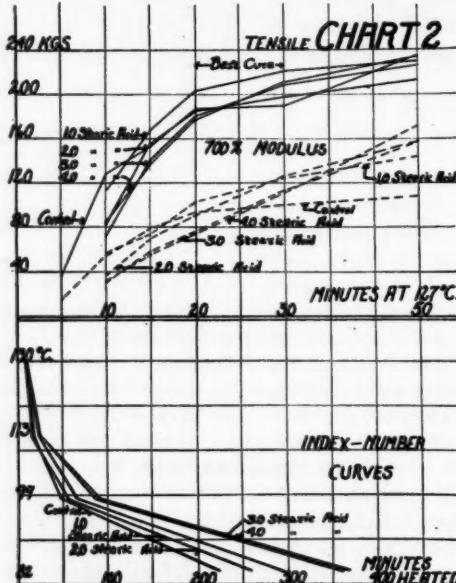
	Parts
Rubber	100
Zinc oxide	10
Hansa yellow	10
Sulfur	3
Mercaptobenzothiazole	1
	124

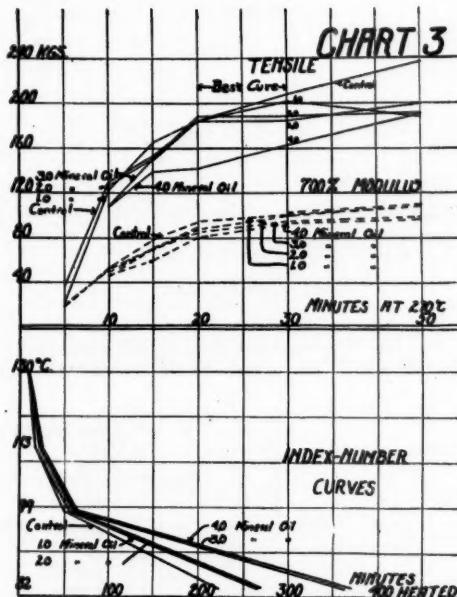
It was used in the master-batch method. Scorch-retarding materials were added to this compound in the amounts of 0.25, 0.50, 0.75, and 1.0 part per 100 parts of rubber; with softeners or activators, 1.0, 2.0, 3.0, and 4.0 parts were used.

In selecting a definite degree of scorch for all comparisons, solubility and swelling tests were made as shown in Figure 1. Here are shown the turbid suspensions of rubber compound in gasoline, and, in corresponding order, the same treated-rubber pellets which have been soaked in gasoline for 2 hours. It is evident that the rubber sample which has been heated for a length of time sufficient to give a 105-mm. height of obscuring column (when immersed in gasoline 15 minutes and shaken 1



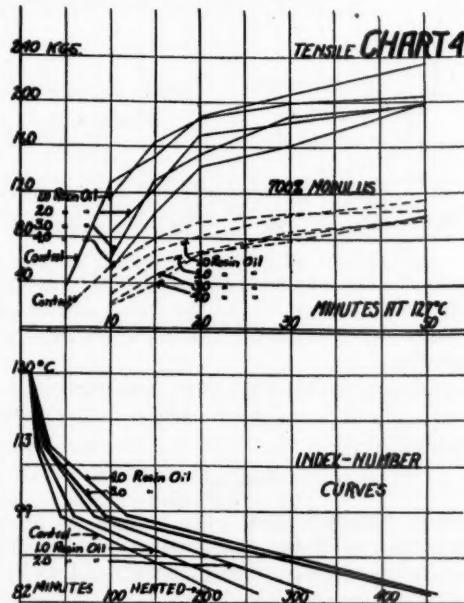
minute) just begins to swell after 2 hours; this indicates set-up, whereas the smooth dissolving as in the case of pellets heated for a shorter time does not. The time necessary to reach this definite degree of scorch is taken as the so-called index number, and it is felt that it represents a sharp duplicable





end point. Particular stress is laid upon the fact that all comparisons in this work are made using this degree of scorch.

In selecting a temperature range for study of scorching, four temperatures were chosen and were obtained by boiling the following liquids in the special container:

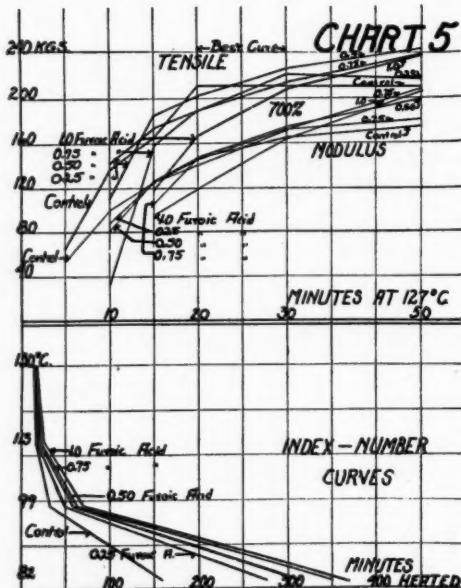


	° C.	° F.
Ethylene dichloride	82	180
Water	99.5	210
Butyl alcohol	113.5	236
Cellosolve	130	266

The first of these temperatures might be considered as close to good milling temperature, the second could be considered as fair milling temperature, while the third would be called a high milling temperature. The fourth temperature tried is slightly above the temperature of cure.

#### Materials Used

Pine tar (2), mineral oil, and rosin oil were used as softeners. The mineral oil was a heavy viscous oil (specific gravity 1.06),



known under the trade name of Para Flux. The rosin oil was a synthetic oil containing 50 per cent rosin and 50 per cent light petroleum oil. Stearic acid was tried as an activator and softener combined.

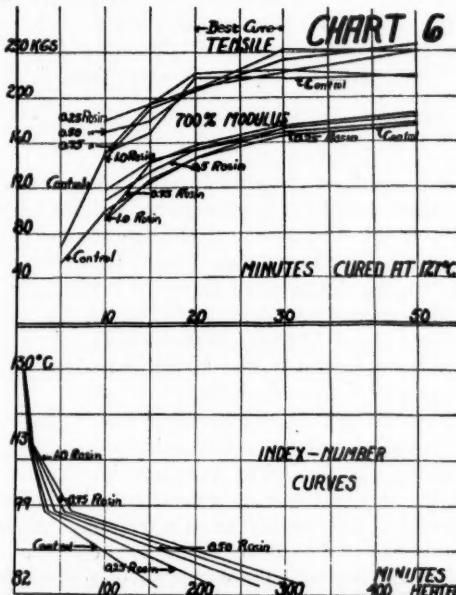
The retarding materials tried were: benzoic acid, *o*-chlorobenzoic acid, glyceryl phthalate, furoic (pyromucic) acid, rosin, and zinc resinate.

#### Results

The results obtained have been plotted in the charts. Tensile strength and 700 per cent modulus values are shown to give an indication of the physical properties of the stock; the index-number curves are plotted from values obtained at the

various temperatures. In Table II a tabulation of these numbers is given after corrections, which are discussed later, have been applied.

Chart 1 shows the effect of various amounts of pine tar. These data show that pine tar has a very definite retarding effect upon scorching at 82°, 99°, and 113.5° C., with little effect at 130° C. Therefore, this material is a scorch retarder of long-standing usage. The index-number curves show graphically the great effect that a difference of 31° C. in milling temperature, for example, would have upon scorchability of these stocks. At 82° C. there is a difference of 256 minutes in scorching time between the control stock and that containing 4.0 parts of pine tar; at 113.5° C. the difference is only 20 minutes. It is also pointed out that the actual time necessary



to scorch the control at 113.5° C. is 17 minutes, while at 82° C., 222 minutes are required. These values for the stock containing 4.0 parts of pine tar are 37 minutes at 113.5° C. and 478 minutes at 82° C.

It is possible from the index-number curves to find the effect of any normal differences in milling or calendering temperatures. For factory scorching indications, it might be well to take a more advanced state of scorch for index-number comparisons. This, of course, could be accomplished by a more severe treatment of the pellet in gasoline.

In Chart 2 the effect of stearic acid is shown. It is evident that this material activates mercaptobenzothiazole and at the same time decreases its scorchability. Three parts of the acid are about as useful for this purpose as are 4.0 parts and repre-

ent a gain in time of scorch of 144 minutes at 82° C. and of only 8 minutes at 113.5° C.

In Chart 3 the effect of a mineral oil, comparable to pine tar in its softening effect, is shown. Its effect on tensile values is the same as that of pine tar, but it softens the modulus to a lesser degree. However, it is also evident that its scorch-retarding effect is not as great, 4.0 parts giving a gain in time of 147 minutes at 82° C. against 256 minutes obtained with 4 parts of pine tar.

The effect of a synthetic rosin oil is shown in Chart 4.

The behavior of a typical scorch-retarding material is shown in Chart 5. Furoic acid (sometimes known as pyromucic acid) is used. From the tensile and modulus properties it is seen that all stocks containing the acid give curves which cross those of the control somewhere in the range of best hand-tear cure, i. e., between 20 and 30 minutes; this indicates that at these points the physical properties of the control are exactly duplicated, and that an increase in scorchiness is obtained, as indicated by the index-number curves. The effect of this material on temperature coefficient of scorch will be discussed later.

The results obtained using WW rosin are shown in Chart 6. Its effect upon scorching is of such magnitude that it was classified as a scorch-retarding material and used as such in small amounts. Its effectiveness is quite good with this type of acceleration, but it does not follow that it will function with an accelerator of another type. Several cases have been observed where a scorch-retarding material works with mercapto-benzothiazole, for example, and is without effect when used with tetramethylthiuram disulfide.

Chart 7 gives the behavior found when zinc resinate was used as a retarding material. It is evident that this material is practically as effective in its action as rosin.

In Chart 8 the behavior of benzoic acid is shown. This material has desirable properties as a retarder. All modulus curves cross those of the control within the best-cure range, as do all tensile curves, with the exception of that of the stock containing 1.0 part. Critical-point curves show decided retarding in scorchiness at all temperatures except 130° C. It is also evident that 0.75 part of the acid is almost as effective as 1.0 part. These stocks set up over 200 minutes slower at 82 degrees than does the control stock.

Chart 9 shows that *o*-chlorobenzoic acid is an effective retarder and can be used in smaller amounts than can benzoic acid, 0.25 part of the former being about equal in retarding action to 0.50 of the latter. Both of the materials tend to act as activators, in so far as modulus values are concerned, giving higher values at the longer cures than the control. If tensile values are considered, it can be seen that benzoic acid tends to give higher values than does the control; with *o*-chlorobenzoic acid the tensile values are not quite so high.

The effect of a material which possesses a violent retarding

effect is shown in Chart 10. Glyceryl phthalate retards scorching very effectively, but it also interferes with cure to such an extent that it would certainly be necessary to use less than 0.25 part on the rubber; in such small amounts it is not as desirable in retarding properties as are some of the other materials discussed.

#### Temperature Coefficient of Scorching

Inasmuch as the index-number values represent the time at which a certain definite and sharp degree of vulcanization exists, it was thought that a calculation of the temperature coefficient of scorch, carried to this particular degree, would be of value and should show a change in temperature coefficient at various temperature increments under 127° C. In making such calculations, the index-number values as observed were corrected for temperature lag so that they represented actual cure equivalents for their respective temperatures. Using a temperature coefficient of 1.50 per 10° F. (5.6° C.), which serves in normal curing practices, the correction values were found as follows:

The actual time-temperature curves were plotted from data obtained by thermocouple measurement, having the thermocouple junction placed in the center of the pellet. From these curves temperature values were taken at small time intervals, and these values were plotted as rates by using the Goodyear  $1/T$  values for the corresponding temperatures. The curves thus obtained were chemical-work or rate-of-vulcanization curves, and the area under them represented the equivalent cure. The difference between the equivalent cure and the total time of cure is given as the correction to be applied at the various temperatures.

TEMP. ° C.	INDEX NO. Minutes	SUBTRACT Minutes
130	5 or over	4
113.5	10 or over	4
99.5	10 or over	4
82	10 or over	3

An interesting observation was that, if the rate of temperature rise of the pellets, when subjected to the foregoing temperatures was plotted, the curves for these temperatures were almost identical, and all pellets were up to the bath temperature in 10 minutes. The same statement as to shape applies to the cooling curves when the tubes containing the pellets were removed from the boiler and cooled in water at room temperature. The time for cooling to room temperature was 8.5 minutes. The previous correction factors also include this value.

Table I gives the temperature coefficients found, using furoic acid as an example and obtaining the rate of change by dividing the corrected index number at 130° C. into that at 113.5° C. for temperature change of 113.5° to 130° C. Then the 113.5° C. values were divided into 99.5° C. values and 99.5° C. values into those found at 82° C.

Table I—Temperature Coefficient of Scorching  
(Rated per 10° C.)

Temperature change, ° C.	82-99.5	99.5-113.5	113.5-130
Increment, ° C.	17.5	14.0	16.5
Theoretical (coefficient 1.5° per 10° F.)	2.04	2.04	2.04
Control (no retarder)	3.07	2.07	2.02
Control + 0.25 furoic acid	3.40	2.74	1.82
0.5 furoic acid	3.22	2.46	1.62
0.75 furoic acid	3.35	2.23	1.92
1.00 furoic acid	3.04	2.16	1.82
Average for furoic acid	3.32	2.45	1.82

The data in Table I show that, if one considers these coefficients as rate-of-change values, the control (mercapto-benzothiazole stock) shows a greater rate from 82° to 99.5° C. than it does at the other two temperature increments, but at these increments of temperature the values are almost the same. They are close to those reported by Park (4) for the temperature coefficient of vulcanization, and are not far removed from the theoretical values. The addition of furoic acid increases the values of the temperature rate of change at the two lower temperature increments, while it is decreased at the higher increment as compared to the control stock. This statement is in line with the data obtained upon the curing

Table II—Corrected Index Numbers

	A	B	C	D
	(AT 82° C.)	(AT 99.5° C.)	(AT 113.5° C.)	(AT 130° C.)
	Min- utes	Min- utes	Min- utes	Min- utes
Control 1	219	4.86	45	3.46
+1.0 stearic acid	255	5.0	51	4.6
2.0 stearic acid	290	4.68	62	3.27
3.0 stearic acid	361	3.87	82	3.9
4.0 stearic acid	363	4.22	86	4.1
1.0 pine tar	340	5.18	66	3.9
2.0 pine tar	423	4.97	85	3.9
3.0 pine tar	444	4.36	102	4.9
4.0 pine tar	475	3.80	125	3.8
1.0 mineral oil	263	5.26	50	3.85
2.0 mineral oil	263	4.75	55	3.05
3.0 mineral oil	360	6.22	58	2.75
4.0 mineral oil	366	6.10	60	2.86
1.0 rosin oil	260	4.73	55	3.23
2.0 rosin oil	327	4.24	77	3.08
3.0 rosin oil	451	5.07	89	3.30
4.0 rosin oil	456	4.08	112	4.0
Control 2	158	5.38	29	3.9
+0.25 rosin	217	6.78	32	3.56
0.50 rosin	268	6.70	40	3.63
0.75 rosin	298	7.46	49	4.07
1.00 rosin	317	5.76	55	4.23
0.25 zinc resinate	238	6.42	37	3.36
0.50 zinc resinate	254	6.20	41	3.73
0.75 zinc resinate	299	6.50	46	4.14
1.00 zinc resinate	327	6.06	54	4.16
0.25 furoic acid	273	5.94	46	3.83
0.50 furoic acid	310	5.64	55	3.44
0.75 furoic acid	347	5.88	59	3.10
1.00 furoic acid	357	5.32	67	3.19
Control 3	227	4.48	50	3.85
+0.25 benzoic acid	324	5.00	64	3.55
0.50 benzoic acid	458	4.94	92	3.53
0.75 benzoic acid	529	4.48	117	3.77
1.00 benzoic acid	529	4.20	125	4.03
0.25 o-chlorobenzoic acid	399	5.24	76	3.62
0.50 o-chlorobenzoic acid	455	5.24	87	3.48
0.75 o-chlorobenzoic acid	523	4.50	117	3.66
1.00 o-chlorobenzoic acid	569	4.00	142	3.95
0.25 glyceryl phthalate	424	4.90	86	3.45
0.50 glyceryl phthalate	499	4.16	120	3.53
0.75 glyceryl phthalate	631	4.16	152	4.11
1.00 glyceryl phthalate	666	3.74	178	3.49

characteristics of the stock and seems to be the manner in which a scorch retarder functions.

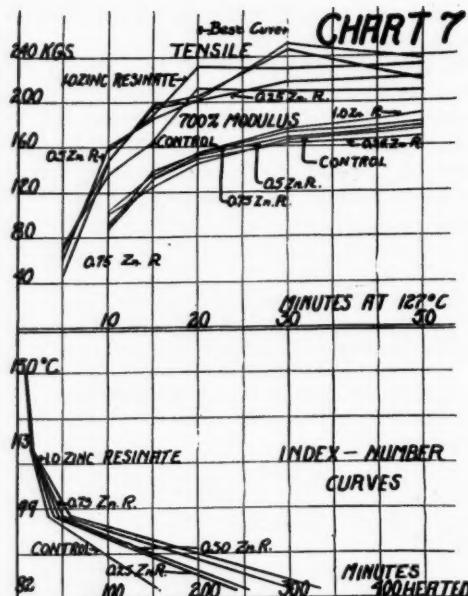
Table II gives the corrected index numbers for all experiments cited and also shows the ratio between these values at various temperatures. These ratios are reduced to a 10° C. rating in Table III.

The values in Table IV offer some interesting comparisons. The three control stocks were of the same formulas but contained different lots of rubber (previously tested and found to cure at the same rate), yet they show different behavior in so far as scorching is concerned.

This variation is not unusual and requires that in this work a control be examined along with each group of experimental compounds. Attention is called to the fact that for the

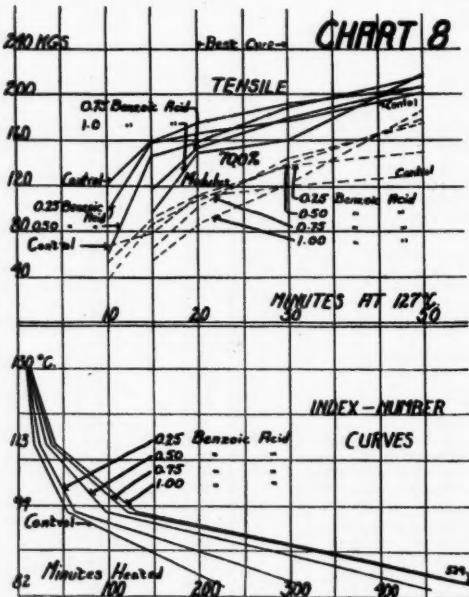
Table III—Temperature Coefficient of Scorching  
(Rated per 10° C.)

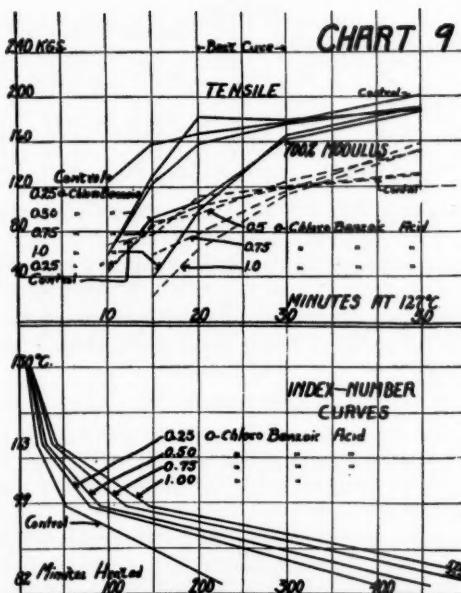
Temperature change, ° C.	82-99.5	99.5-113.5	113.5-130
Range, ° C.	17.5	14.0	16.5
Control 1	2.76	2.47	1.97
+1.0 stearic acid	2.86	3.28	1.68
2.0 stearic acid	2.67	2.33	2.30
3.0 stearic acid	2.21	2.78	2.12
4.0 stearic acid	2.41	2.93	2.12
Average	2.54	2.85	2.05
1.0 pine tar	2.95	2.79	2.56
2.0 pine tar	2.83	2.79	2.22
3.0 pine tar	2.49	3.50	2.12
4.0 pine tar	2.17	2.71	2.50
Average	2.62	2.95	2.10
1.0 mineral oil	3.0	2.74	1.97
2.0 mineral oil	2.71	2.18	2.72
3.0 mineral oil	3.55	1.96	2.54
4.0 mineral oil	3.48	2.04	2.54
Average	3.19	2.48	2.44
1.0 rosin oil	2.70	2.31	2.06
2.0 rosin oil	2.43	2.20	2.63
3.0 rosin oil	2.90	2.36	2.72
4.0 rosin oil	2.33	2.86	2.42
Average	2.59	2.43	2.46
Control 2	3.07	2.07	2.02
+0.25 rosin	3.87	2.54	1.82
0.5 rosin	3.83	2.58	2.23
0.75 rosin	4.26	2.90	2.44
1.00 rosin	3.28	3.53	1.96
Average	3.81	2.86	2.16
0.25 zinc resinate	3.66	2.40	2.22
0.50 zinc resinate	3.54	2.66	2.22
0.75 zinc resinate	3.71	2.96	2.22
1.00 zinc resinate	3.47	2.97	1.98
Average	3.81	2.75	2.11
0.25 furoic acid	3.40	2.74	1.82
0.50 furoic acid	3.22	2.46	1.62
0.75 furoic acid	3.35	2.23	1.92
1.00 furoic acid	3.04	2.16	1.82
Average	3.32	2.45	1.82
Control 3	2.56	2.75	1.97
+0.25 benzoic acid	2.86	2.53	2.18
0.50 benzoic acid	2.83	2.52	2.63
0.75 benzoic acid	2.56	2.70	2.68
1.00 benzoic acid	2.40	2.87	2.65
Average	2.66	2.66	2.54
0.25 <i>o</i> -chlorobenzoic acid	2.99	2.58	2.12
0.50 <i>o</i> -chlorobenzoic acid	2.99	2.48	2.17
0.75 <i>o</i> -chlorobenzoic acid	2.57	2.61	2.73
1.00 <i>o</i> -chlorobenzoic acid	2.28	2.82	2.42
Average	2.71	2.62	2.36
0.25 glyceryl phthalate	2.80	2.46	2.52
0.50 glyceryl phthalate	2.38	2.52	2.57
0.75 glyceryl phthalate	2.38	2.95	2.24
1.00 glyceryl phthalate	2.14	2.48	2.55
Average	2.42	2.60	2.47



simple mercaptobenzothiazole control stock the average coefficient at 82-99.5° C. is decidedly greater than for the other two differences in temperature studied.

The agreement of values found for a single group of stocks, containing different amounts of the same scorch-retarding





material, is not good and may demonstrate the fact that the compounds are dissimilar. However, if these values are averaged, there is a definite trend which shows that the temperature coefficient of scorching decreases in value as the temperatures are raised, and most of the materials tend to give greater rate of decrease than does the control stock.

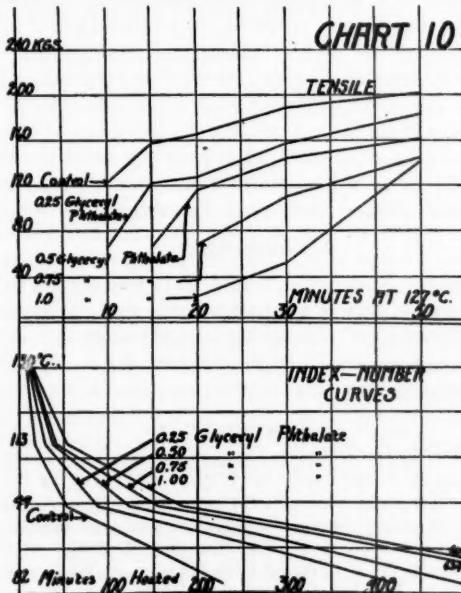


Table IV

CON- TROL	CORRECTED INDEX NUMBERS				TEMPERATURE COEFFICIENT OF SCORCHING			
	82° C.	99.5° C.	113.5° C.	130° C.	82- 99.5° C.	99.5- 113.5° C.	113.5- 130° C.	
	Min.	Min.	Min.	Min.				
1	219	45	13	4	2.76	2.47	1.97	
2	156	29	10	3	3.07	2.07	2.02	
3	227	50	13	4	2.56	2.75	1.97	
				Average 2.70		2.43	1.99	

It should also follow that the increment of temperature which gives the greatest difference between the control stock and that of a stock containing scorch-retarding material is the temperature range in which the retarding material functions most efficiently. This, however, does not necessarily mean that this is the range in which the retarder is most useful for practical purposes.

#### Conclusions

Softeners, such as pine tar, rosin oil, and mineral oil, are useful when scorching trouble is encountered, owing to their scorch-retarding properties as well as to the fact that they soften the rubber batch.

Stearic acid functions as a scorch-retarding material as well as an activating material when used with mercaptobenzothiazole.

A decided gain in scorching time is demonstrated by use of scorch-retarding material without alteration to a great extent of the physical properties of the compound used.

There is a definite change in the temperature coefficient of scorching encountered between 82° and 130° C., this coefficient being greater when rated per 10° C. for the temperature change between 82° and 99.5° C. than it is either between 99.5° and 113.5° C., or between 113.5° and 130° C.

There is a tendency on the part of the stocks containing some retarders to give a greater percentage decrease in temperature coefficient of scorching over the range studied than does the control stock. With other retarding materials this does not hold.

A scorch-retarding material is best measured by its effect upon index numbers of a control stock rather than by its effect upon the temperature coefficient of scorching.

#### Acknowledgment

The author wishes to thank A. J. Crawford for work done on measurement of rate of temperature rise and fall and calculation of theoretical temperature coefficients of scorching. Thanks are also due L. B. Sebrell and R. P. Dinsmore for permission to publish this paper.

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## Behavior of Rubber under Repeated Stresses<sup>1,2</sup>

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This paper describes a simple and convenient apparatus for obtaining a graphical record of the tensile properties of rubber under a variety of conditions of stressing. Data are given showing the effect of repeated stretching and the speed of stretching on the stress-strain properties of typical rubber compounds. The recovery of rubber from strain is considered, and it is observed that complete recovery does not take place. Conclusions are drawn regarding the practical use of stress-strain curves in evaluating rubber compounds. The present paper does not consider the retraction cycle of the stress-strain curve, nor the energy relations involved. No theoretical explanation is offered at this time for phenomena described.

**T**HIS paper describes some of the effects of repeated stressing on the tensile properties of rubber. The fact that the properties of rubber are influenced by stretching or other mechanical treatment is not new. Data have been given by Buasse and Carrière (2), Shedd and Ingersol (9), Schwartz (7), Beadle and Stevens (1), Scoble (8), Gurney and Travener (5), and others. All of these authors point out that changes take place in the physical properties of rubber on stretching. Williams (11) has suggested stretching rubber samples a few times to reduce "plastic flow" on subsequent tests. Gerke (4) has described "equilibrium stress-strain curves" which were obtained from samples which had been stretched several hundred per cent and caused to vibrate while under tension. After this treatment his data show that stress-strain curves, up to certain elongations, can be obtained without appreciable hysteresis.

<sup>1</sup> Received September 10, 1931. Presented before the Division of Rubber Chemistry at the 82nd Meeting of the American Chemical Society, Buffalo, N. Y., August 31 to September 4, 1931.

<sup>2</sup> Published by permission of the Director, U. S. Bureau of Standards.

In the present paper some of the work of previous investigators has been repeated, except that modern compounds have been employed and tests conducted at relatively high speeds. By the use of apparatus, which was developed and is described, extension and retraction curves can be made autographically in less than one second, although for most purposes a somewhat slower speed is recommended. Repeated stress strain curves up to 100 or more successive cycles can be recorded with facility. The behavior of different types of rubber under repeated stress is illustrated in this paper, and the recovery of rubber from strain is considered.

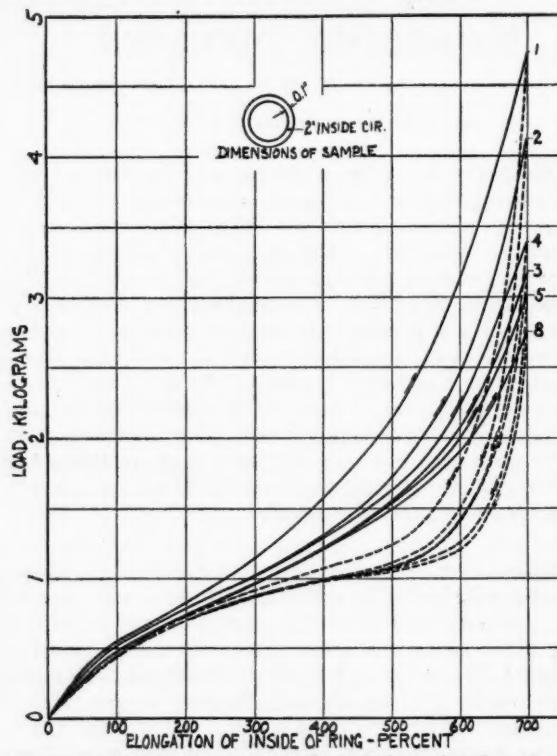


Figure 1—Various Stress-Strain Records from One Sample of Pure Gum Rubber  
Numerals indicate order in which curves were recorded.

The way in which the stress-strain curve of a sample of rubber is affected by its previous strain history is illustrated in Figure 1.

These curves were derived by stretching the same sample of rubber to an elongation of 700 per cent and return eight times. They were recorded in the order shown by the numerals. A brief rest period caused the apparent discrepancy in the location of curves 3 and 4. Two additional curves might have been recorded between 5 and 8 but were omitted to avoid confusion. The curves shown do not by any means represent the whole

range of possible stress-strain curves from a given sample of rubber. A rubber which contains considerable compounding material is apt to show a much wider range, and, as will be shown later, consecutive strains of different values may produce quite unusual results.

#### Multiple-Cycle Stress-Strain Recorder

The apparatus used for making successive stress-strain determinations of samples of rubber compounds is illustrated in Figure 2.

The sample for test (usually ring-shaped) is placed around the pin grips at *A* and is stretched by movement of the slide, *C*, which is actuated by crank *B*. The tension in the sample is transmitted through the calibrated spring, *D*, to the recording arm, *H*. As crank *B* moves, causing sample to stretch, crank *E*, by means of a flexible wire and rubber band, *K*, causes recording plate *G* to move back and forth at right angles to the direction of tension, and thus point *H* traces a stress-strain record. Adjustment lever *F* is used to stop the movement of the recording plate when desired and also to adjust the position of the recording plate relative to the recording point.

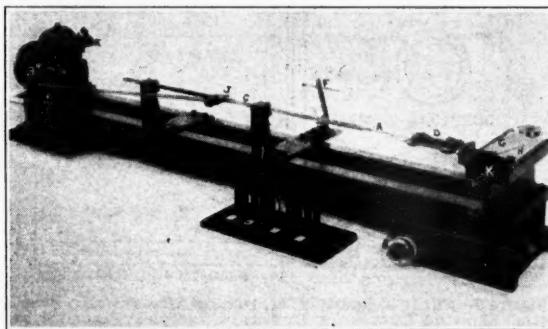


Figure 2—Apparatus for Recording Stress-Strain Properties of Rubber

A common speed of operation for the machine is 30 cycles per minute. It may, however, be run as fast as 100 cycles per minute and, by the use of reduction gears, to as low a speed as desired. Suitable springs are provided so that the maximum capacity may be set at values between 2 and 20 kilograms. The length of stroke or the stretch may be set at any amount up to 10 inches (25.4 cm.) by adjustment in the slotted crank arm at *B*. The initial position of the slide, *C*, may be adjusted by means of set screw *J*.

The stress-strain relation is recorded on stylograph paper by a slight pressure of a steel point at *H*. The recorded curves, although adequate for many purposes, are not drawn to truly rectangular coördinates. In order to transfer results to rectangular coördinates, a calibrated glass template, corresponding to the spring used, is employed in conjunction with the proper elongation scale. For precise work a correction may be made for the compression of the spring.

Ring samples cut from sheets with a die were used in the work described. Results may be obtained with these samples

which are adequate for many purposes. However, these rings have the obvious disadvantage that the outside and the inside are under different degrees of strain when the sample is stretched.

In some work not reported, two other types of samples were used: straight strips held in grips; and thin rings cut from a tube formed on a mandrel by deposition. The former are satisfactory for low elongations where the concentration of stresses at the grips is not important. The latter have advantages over rings cut from sheets in that the inside and outside diameters can be made more nearly equal. The type of grip described by Hahn and Dietrich (6) could probably also be adapted to this machine.

#### Effect of Speed of Stressing

One of the purposes in constructing the apparatus described was to record stress-strain properties at higher rates than are ordinarily used. Data on the influence of the rate of stretch

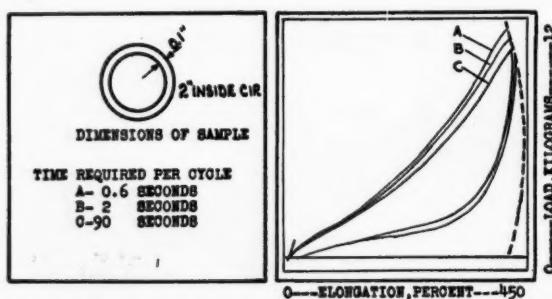


Figure 3—Effect of Speed of Stretch on Stress-Strain Properties, Showing Curves for Duplicate Samples Recorded at Three Different Speeds

on the stress-strain relations were determined by tests of duplicate samples at widely different speeds. Typical records which show the effect of speed as well as the rapidity with which curves can be recorded are illustrated in Figure 3.

Complete hysteresis curves up to 450 per cent elongation were made at each of three speeds. Curve C corresponds to about the usual testing speed;<sup>3</sup> curve A, to a speed 150 times as great. Curve B was drawn at an intermediate speed of 30 cycles per minute. As the speed of stretch increases, the load for corresponding elongations increases; but over the range shown, differences due to speed of stretch are not very great.

These conclusions are consistent with the results reported by Buasse and Carrière (8), by the Bureau of Standards (9), and by Somerville, Ball, and Edland (10). All of these publica-

<sup>3</sup> The ordinary speed of testing for dumb-bell samples is 20 inches (51 cm.) per minute rate of jaw separation. With the multiple-cycle stress-strain recorder the rate of stretch follows approximately a simple harmonic law and varies throughout the stroke, so that it is difficult to make a direct comparison.

tions, however, deal with testing speeds slower than used in the present work.

High-speed stressing apparently offers no particular advantage for vulcanized-rubber compounds, aside from the saving in time. With unvulcanized specimens, however, where testing at the ordinary speeds is impractical, high speeds may give results quite comparable to those obtained with vulcanized specimens. In the results presented in this paper, a speed of 30 cycles per minute was used.

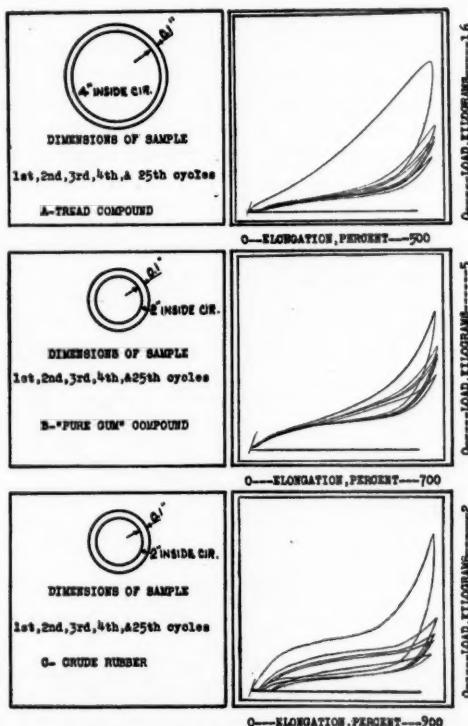


Figure 4—Charts from Stress-Strain Apparatus, Showing Successive Cycles as Recorded for Three Types of Rubber

#### Successive Stress-Strain Curves

Figure 4, which is taken directly from chart records, shows the results of making several stress-strain determinations in succession on the same rubber sample. The three sets of curves were made with three types of rubber (the compositions of which are shown in Table I), and in each case were carried almost to the breaking point. *A* is a tread stock containing about 20 per cent volume of carbon black; *B*, a pure gum stock; and *C*, crude rubber cut from a sheet of evaporated latex.

Table I—Compounds Used in Tests

INGREDIENT	PARTS BY WEIGHT	
	Tread compound (A of Figure 4)	Pure gum compound (B of Figure 4)
Rubber	100.0	100.0
Sulfur	3.5	3.0
Zinc oxide	20.0	5.0
Carbon black (Micronex)	30.0	...
Stearic acid	2.0	...
Age Rite	1.0	...
D. O. T. G.	1.25	...
"Tuads" (tetramethylthiuram disulfide)	...	0.25

It will be noted that the general form of each series of curves is the same, and that the greatest difference occurs between the first and second cycles. These records are typical of those from all rubber stocks tested. The fact that the curves start slightly above the zero line is due to the load required to bend the sample from the circular to the elongated position. The change which is produced in any particular rubber by stretching is more apparent the higher the elongation, but it is evident at relatively low elongations.

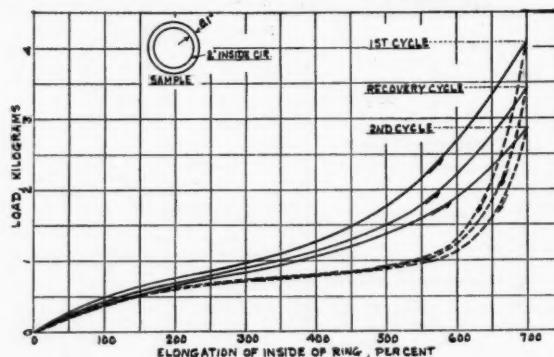


Figure 6—Recovery of Ring Sample of Pure Gum Rubber after Strain  
Recovery curve shows effect of 24 hours at room temperature.

It is probable that some of the change between successive cycles in stretching rubber is due to a temperature increase in the sample itself, owing to stressing. However, it will be evident from results shown that the temperature effect is secondary to changes in the physical character of the rubber.

#### Recovery from Strain

If a sample of rubber is stretched a series of times and then allowed to rest for a period, the rubber will recover its stress-strain characteristics to a degree, and a subsequent stress-strain curve will lie intermediate between the first and last of the series. Recovery may be hastened by the application of heat, but complete recovery does not take place. Figure 5 illustrates the recovery of a tread stock after stretching. The first and fifth cycles are shown, and also curves after partial recovery. Apparently, curve A represents the limit

of recovery, unless heating is carried on for a sufficient period to cause increased vulcanization.

Figure 6 shows similar curves for a pure gum compound. Recovery in this stock is much more rapid than in a tread stock. The intermediate curve represents the apparent limit of recovery.

The persistence of the effect of an initial strain in rubber on its subsequent stress-strain characteristics is illustrated in Figure 7. Samples of tread compound, half of which had been given an initial stretch of 500 per cent, were placed in an oven at 70° C., and stress-strain curves determined on both stretched and unstretched samples at intervals up to 12 days. From these curves, loads at different elongations were determined and are plotted.

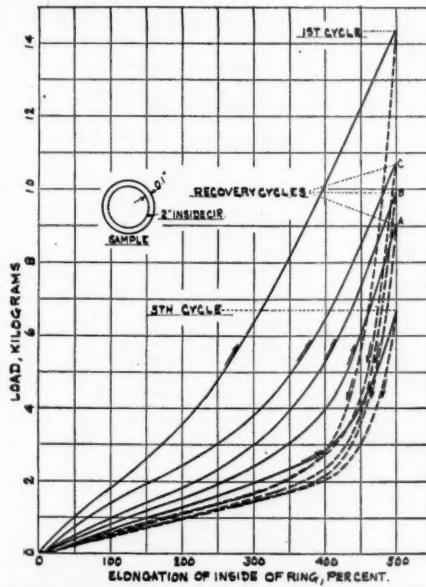


Figure 5—Recovery of Ring Sample of Tread Compound after Strain

Curve A—Effect of 2 hours' rest at room temperature  
 Curve B—Effect of 10 minutes at 100° C.  
 Curve C—Effect of 45 minutes at 100° C. and 40 hours at room temperature

Referring to the 500 per cent load curves, it will be noted that the initial load required to produce this elongation of the unstretched sample was 10 kg., while that for the stretched sample was 6.6 kg. Two days at 70° C. indicates a restoration of the original condition (curve A'), but that this is an aging effect rather than recovery is illustrated by a corresponding increase in the 500 per cent load of the sample not initially stretched. Throughout the 12-day period, curve A' with lower load values parallels curve A and illustrates the persistence of the initial-strain effect. The same may be said of curves B and B', C and C', D and D', and E and E', which

show comparative loads at other elongations. Figure 8 is similar to Figure 7, and shows comparative results obtained with stretched and unstretched pure gum samples. The difference between the strained and unstrained samples is not as great as is shown in the tests of the tread compound, and recovery is more rapid. The effect of the initial strain, however, is evident throughout the heating period by the lower loads obtained for samples initially stretched.

It is interesting to note in these tests that, from the standpoint of accelerated aging, the initially stretched samples and the unstretched samples behaved in almost identically the same manner; that is, whatever change was produced by stretching had no effect on the aging properties.

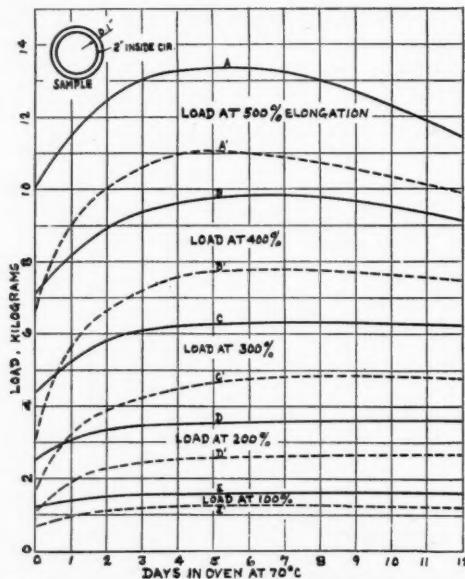


Figure 7—Persistence of Effect of Strain in Tread Compound through Accelerated Aging

Broken lines show results from samples initially stretched 500 per cent and immediately released; full lines show results from samples not initially stretched.

Another test showing the persistence and the extent of a strain effect consisted in subjecting samples to relatively small distortion and noting the effect on the subsequent stress-strain curves. Six rings of the same tread compound were taken; one was used for reference and the other five given one stretch of 100, 150, 200, 250, and 300 per cent, respectively, and immediately released. They were allowed to rest for 24 hours and then stress-strain determinations were made. The results are shown in Figure 9. It will be noted that the lower part of the curves are quite widely separated and that each curve has a break approximately at a point correspond-

ing to its initial elongation, after which the rubber tends to follow the curve of the reference sample. In fact, if the upper part of the curves only were shown, the conclusion would be reached that the samples were unaffected by small strains. The moduli at lower elongations, however, are quite different. In order to determine if successive elongations of relatively low values would show a greater effect and also alter the upper part of the stress-strain curve, a test was made by repeating the initial strains 100 times before making stress-strain determinations. The results were similar to those shown in Figure 9, except that the effects of the initial strains were emphasized. It appears that the changes produced by stretching this type of rubber compound are progressive, each increase in stretch producing additional changes. Under decreasing loads all samples showed practically identical characteristics.

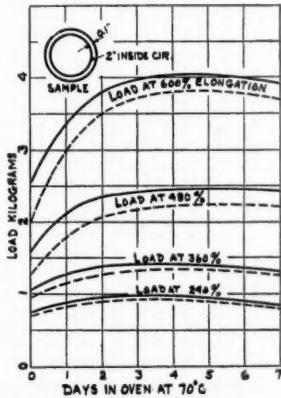


Figure 8—Persistence of Effect of Strain in Pure Gum Rubber through Accelerated Aging

Broken lines show results from samples initially stretched 600 per cent and immediately released; full lines show results from samples not initially stretched.

With a pure gum compound the progressive effect of strain is not as pronounced as in a tread compound. It appears rather that a small initial strain affects the whole of the stress-strain curve.

#### Remarks

The data given show the elusive character of the stress-strain curve of rubber. The initial-stretch curve, which is ordinarily used in evaluating a rubber compound, is possibly the most definite but it is interesting to note that it is the curve least permanent in character. It apparently cannot be retraced after the rubber has once been stretched. If the stress-strain curve is to be used in designing rubber compounds for specific purposes, it is obvious that the conventional curve may not give the proper stress-strain relations.

A study of the phenomena encountered in the repeated stressing of rubber, taking into consideration different compounding ingredients, different degrees of vulcanization, etc., should throw light on the structure of rubber compounds and on the behavior of different compounding ingredients in them. This work indicates that the lower part of the stress-strain curve, which is seldom accurately determined, may have an important bearing on the real properties of a compound.

The apparatus described was constructed primarily for investigational studies, but the speed and ease with which a stress-strain record of a rubber sample is made suggests the

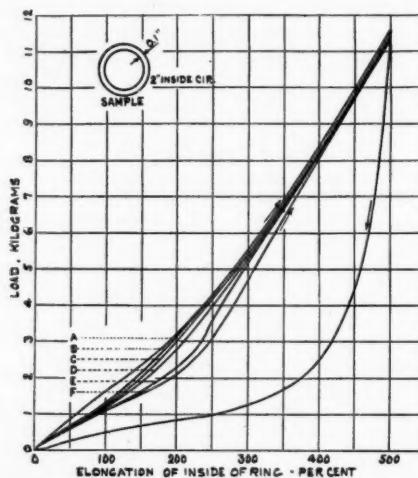


Figure 9—Effect of Initial Small Strains of Samples of Tread Compound on Subsequent Tensile Properties

Curve A, no initial stretch; curve B, 100 per cent initial stretch with immediate release; curve C, 150 per cent initial stretch with immediate release; curve D, 200 per cent initial stretch with immediate release; curve E, 250 per cent initial stretch with immediate release; curve F, 300 per cent initial stretch with immediate release. Return curves same for all samples.

use of a machine of this type for certain classes of routine testing.

### Conclusions

The stress-strain relations of a sample of rubber are very markedly affected by the previous strain history.

Rubber will recover to some extent from the effects of a strain, but not completely.

In a rubber compound, such as tread stock, a series of increasing strains has a pronounced progressive action, each increase in strain producing added effects.

The conventional stress-strain curve does not represent the permanent characteristics of a rubber compound.

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## Some Factors Affecting the Resistance to Flexing<sup>1</sup>

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Failure on flexing has been shown to be due to oxidation rather than mechanical fatigue or the action of ozone.

The action of secondary aromatic amines of the type of phenyl- $\beta$ -naphthylamine in retarding the failure of rubber on flexing lies in their antioxidant properties.

WITHIN the last few years the deterioration of vulcanized rubber under dynamic strain has received considerable attention from the rubber industry. The cracking of tire treads, carcass, and belting separation, the cracking of boot uppers and shoe soles are types of failure which come in this class.

In order to study this type of deterioration it is necessary to have a quick method of laboratory evaluation. To meet this need, a large number of the rubber manufacturers have developed flexing machines, many of which are designed to make only specific tests. In addition, there are several general-duty flexing machines, for example, the De Mattia, the Torrence-Peterson, the du Pont, and the United States Rubber Company machines. All of these are designed to duplicate in the laboratory in a short period of time the same conditions which the article must withstand in service.

Although a great deal of work has been done on the utilization of the flexing test, very little has been published on the causes underlying this failure. In general, three causes for the failure of rubber on flexing have been proposed: first, mechanical fatigue (which is defined as that failure produced

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by the action of repeated stresses on the rubber itself, and not that produced by the cutting or chafing action of compounding ingredients on the rubber); second, oxidation; and third, the action of ozone. The first two causes proposed, mechanical fatigue and oxidation, are obvious in their origin. The third, the action of ozone, has been based on the fact that when rubber is flexed rapidly it is possible to detect an electric charge which might be sufficient for the production of ozone, and furthermore, the small nicks or cracks, whose appearance characterizes the failure of rubber on flexing, bear considerable resemblance to the cracks produced when stretched rubber is exposed to ozone.

All of the tests made in the work described in this paper were carried out on the small du Pont flexing machine, which

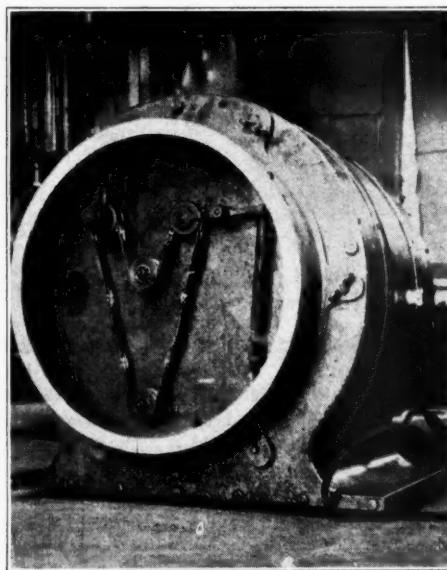


Figure 1—Small du Pont Flexing Machine

is illustrated in Figure 1. This machine was selected because it is designed with an air-tight glass front so that the belt may be flexed in any gas medium desired. When carrying out the test, a slow stream of the gas being used is passed through the chamber, thus giving a positive assurance that a sufficient and relatively uncontaminated supply of the gas desired is always present in the chamber. The principle of this machine is the same as that of the larger one previously described (3) and consists of flexing a belt comprised of molded rubber links backed with cord fabric over a series of pulleys.

The failure of the sample is indicated by the appearance of small nicks which soon increase in size until they become deep cracks often extending all the way across the test piece.

In general, these nicks appear in several of the transverse grooves at the same time, and at the completion of the test they will be found in practically all of them. The resistance to flex cracking is judged both by the time necessary for these cracks to appear and by the condition of the samples after the appearance of the cracks.

If mechanical fatigue is primarily responsible for the deterioration of rubber on flexing, then varying the concentration of oxygen in the chamber in which the sample is flexed would not be expected to change the time required for development of cracks very materially. On the other hand, if oxidation or the action of ozone is responsible for the failure, then changing the concentration of oxygen or ozone in the flexing chamber would be expected to have a marked effect on the time for failure to take place.

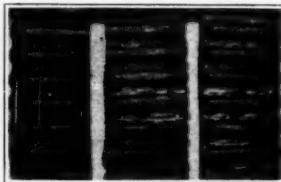


Figure 2—Samples after 64 Hours' Flexing in Varying Concentrations of Oxygen

#### Flexing in Varying Concentrations of Oxygen

In order to study the effect of varying the concentration of oxygen on the rate of failure, the two following high-grade tread stocks were prepared:

Smoked sheets	100	100
Zinc oxide	10	10
Carbon black	40	40
Stearic acid	2	2
Pine tar	4	4
Sulfur	3.375	3.375
Butyraldehyde-aniline <sup>a</sup>	0.875	0.875
Phenyl- $\beta$ -naphthylamine	...	1.25

<sup>a</sup> The butyraldehyde-aniline condensation product known as accelerator "808" was used.

Phenyl- $\beta$ -naphthylamine was chosen as the antioxidant because of its availability, and because it is a typical example of the secondary aromatic amines which have proved very effective in increasing the service life of rubber exposed to this type of strain.

Belts composed of five links of each of these two compounds were flexed in an atmosphere of nitrogen, air, and oxygen. In the case of the flexing tests in nitrogen and oxygen, the air in the flexing chamber was displaced by passing approxi-

mately six volumes of gas through the flexing chamber before starting the test. A slow stream of the gas being used was passed through the chamber throughout the course of the test, and after each examination of the belt the chamber was flushed out before proceeding. The nitrogen was obtained from a cylinder of the compressed gas and was washed by bubbling through an alkaline sulfite solution before passing it into the flexing chamber. No effort was made, however, to remove the oxygen dissolved in the rubber. The source of supply of oxygen was an ordinary commercial cylinder of the compressed gas and it was not further purified. The only precaution taken in the test in air was to run a slow stream of air through the chamber during the course of the test.

The results of these tests in varying concentrations of oxygen, in which the degree of failure from none to badly cracked is expressed by numbers 0 to 8, are given in Table I.

Table I—Flexing in Varying Concentrations of Oxygen

TIME OF FLEXING Hours	NITROGEN		AIR		OXYGEN	
	Blank	Anti- oxidant	Blank	Anti- oxidant	Blank	Anti- oxidant
10	0	0	0	0	0	0
20	0	0	1	0	1	0
30	0	0	3	0	3	0
40	0	0	4	1	5	1
50	0	0	6	2	6	3
60	0	0	7	3	7	4
75	0	0				
100	1	1				
125	2	1				
150	3	2				
175	4	3				
200	7	6				
225	8	7				

The appearance of these samples is shown in Figures 2 and 3. In order to show up the cracks to a better advantage the samples were dusted with zinc oxide before photographing. Figure 2 shows the samples after 64 hours of flexing in varying concentrations of oxygen. Sample 1 was flexed in nitrogen, sample 2 in air, and sample 3 in oxygen.

Figure 3 shows the effect of phenyl- $\beta$ -naphthylamine. Sample 4 is the stock containing no antioxidant after 40 hours of flexing in air. Sample 5 is the same stock with 1.25 per cent of antioxidant added. Sample 6 is the stock containing no antioxidant and sample 7 the stock containing antioxidant after 225 hours of flexing in nitrogen.

Two facts are rather distinctly shown by this series of tests in varying concentrations of oxygen. First, phenyl- $\beta$ -naphthylamine shows practically no protection when the test is run in nitrogen. Second, increasing the concentration of oxygen above that present in air at atmospheric pressure has only a slight effect on the rate of deterioration.

The fact that when the flexing was carried out in nitrogen an extremely long time was required to cause failure, 225 hours instead of the 60 hours required when the flexing was carried out in air, indicates that some factor other than mechanical fatigue must be the primary cause of failure. If oxidation

is an important factor in failure on flexing, then the effectiveness of phenyl- $\beta$ -naphthylamine probably lies in its retarding action on oxidation, and no effect would be expected from this antioxidant in the absence of oxygen. The test run in an atmosphere of nitrogen seems to substantiate this viewpoint. The very slight retarding action shown by phenyl- $\beta$ -naphthylamine is undoubtedly due to the fact that the sample flexed contained some oxygen dissolved in the rubber and adsorbed on the pigments used in compounding. When the test is carried out in either air or oxygen, however, a marked superiority is noted in the stock containing the antioxidant.

When the flexing test was carried out in oxygen, the rate of deterioration was approximately the same as when the test was carried out in air. Marzetti (1) has shown that 1.0 per cent of oxygen is sufficient to destroy the physical properties of rubber. Williams and Neal (4) have shown that at 37° C., the temperature at which these tests were carried out, the solubility of oxygen in rubber is greater than 1.0 per cent. These same investigators have further shown that the combination of oxygen with rubber in a closed system pro-

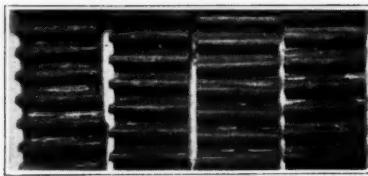


Figure 3—Effect of Phenyl  $\beta$ -Naphthyl-  
amine

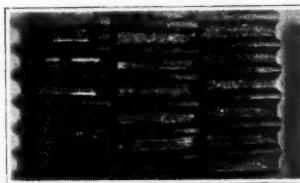
ceeds at a uniform rate until the available oxygen is reduced below the amount present in air at atmospheric pressure. Thus, at the temperature of the test, the concentration of oxygen dissolved in the rubber when flexed in air is sufficient to maintain the oxidation at a maximum rate, and the amount is sufficient to cause a failure of the rubber. In view of these facts, no great increase in rate would be expected when the concentration of oxygen is increased over that present in air at atmospheric pressure.

#### Flexing in Ozone

In order to determine whether ozonization were playing a part in the failure, a test was run in which ozone was introduced into the flexing chamber. The ozone was produced by passing a stream of air through a Cottrell ozonizer and then into the chamber. In order to test for the presence of ozone in the chamber, pieces of rubber stretched 15 per cent were placed inside the chamber. The concentration of ozone was such that the test pieces were checked in thirty minutes.

The belt was examined every hour throughout the test. When the test had been run for two hours, very fine checks were apparent in both the stock containing antioxidant and the one without antioxidant. These checks gradually increased in each sample as the test progressed. The test was continued for thirty hours, when the checks had increased greatly and extended over the entire surface of the sample. The appearance of these samples at the conclusion of this test is shown in Figure 4, in which sample 8 is a stock containing no antioxidant after 40 hours of flexing in air, and samples 9 and 10 are, respectively, stocks with and without antioxidant after 30 hours of flexing in ozone.

It can be seen from this test that in the presence of ozone phenyl- $\beta$ -naphthylamine does not protect the rubber. It was also very noticeable as the test progressed that the checks appearing on the sample differed from those produced when the flexing was carried out in air or oxygen. The nicks were very much shallower than those in air, and they also seemed to be more of a surface crack than a true flexing nick. While



8            9            10  
Figure 4—Results of Flexing in  
Ozone

this test had indicated that ozone was not a factor in the failure of rubber on flexing, one further test was made to check this observation. If ozone is produced when flexing is carried out in air or oxygen, it should be possible to detect it. Probably the most sensitive means of detecting ozone is by its action on stretched rubber, since this action appears to be cumulative (2). Accordingly, the flexing test in air was repeated and pieces of rubber stretched 15 per cent were hung inside the chamber so that their surface was within 1 cm. (0.3937 inch) of the belt where it passed over one of the pulleys. This test piece remained in position for the entire 40 hours of flexing. At the completion of the test when the blank was badly nicked and the protected stock had just begun to show one or two very slight nicks, the stretched test pieces were carefully examined, but they did not exhibit the slightest trace of checking such as that produced by the action of ozone.

This test indicates that no ozone is produced when the flexing is carried out in air. Tests in this laboratory have indicated that the charge produced on flexing vulcanized rubber is comparatively small and a more rapid rate of flexing than

that given by this flexing machine is probably required for production of ozone. It is also possible that the machine was well enough grounded to dissipate any charge before ozone could be produced.

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